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Final Technical Report

from

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Investigation and Development
of Advanced Surface Microanalysis
Techniques and Methods

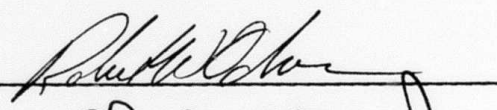
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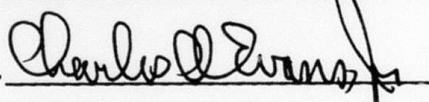
Defense Advanced Research Projects Agency (DoD)

DARPA Order #4713

Under Contract #MDA903-83-C-0099 issued by Department of the Army,
Defense Supply Service-Washington, Washington, DC 20310

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Effective Date: April 1, 1983

Expiration Date: September 30, 1985

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EXECUTIVE SUMMARY

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EXECUTIVE SUMMARY

The successful development of advanced materials systems and devices depends strongly on sensitive quantitative materials characterization provided by surface microanalytical techniques. At the present time, the materials systems under development or envisioned for the near future are at or beyond the capabilities of state-of-the-art materials characterization techniques and methodologies. If these new materials development programs are to be successful, a parallel effort to advance existing microanalytical techniques and to develop next generation analytical capabilities must be initiated.

TASK OBJECTIVES

The objective of this research program was to advance the performance capabilities of surface microanalytical techniques in order to meet the current, near term and future materials characterization demands of advanced materials development programs.

The goals of this research program were two-fold:

1. Improve the sensitivity and quantitative capabilities of existing surface microanalysis techniques operating in the 1 to 150 micrometer lateral dimension regime; and
2. Investigate and evaluate techniques for obtaining trace level analyses of materials down to the 0.1 micrometer lateral dimension.

TECHNICAL RESULTS

This research program produced several results in the advancement of quantitation and detection limits of the two most widely used microanalytical techniques, scanning Auger microscopy (SAM) and secondary ion mass spectrometry (SIMS). The major advance in quantitation of these techniques was achieved by using large area techniques which are capable of accurate bulk or depth profiling analyses to prepare standards for microanalytical depth profiling by either SAM or SIMS. This concept was developed and tested on the characterization of borophosphosilicate glass (BPSG) passivations and intermetal dielectrics. The use of bulk analysis techniques to quantify the composition of standards has been subsequently applied to several technology development projects and is being used by other researchers to quantify standards for other analytical techniques and methods.

Three approaches were evaluated for the improvement of trace element detection limits. The first was to determine whether the laser enhancement concepts of resonant and nonresonant multiphoton ionization (MPI), processes which have demonstrated very high ionization efficiencies in pulsed laser systems, could be adapted to continuous wave (CW) operation. Although CW laser ionization schemes could provide a very significant enhancement in trace component analysis, we recognized from the outset of this work that only selective elements might demonstrate this enhancement because of the rather limited photon energy and/or wavelengths available from current CW laser systems. Our investigation of CW laser-assisted ionization of Hg sputtered from a HgTe matrix did not demonstrate a measurable enhancement of the Hg ion signal; however, this research did lead to a more complete understanding of ion production from HgCdTe which was thoroughly investigated in another research program funded by DARPA.

The second approach to improved trace element detection limits was to thoroughly evaluate the analytical methodologies of specific impurity/matrix combinations relating to a particular technology. The two most successful studies resulting from this approach were the development of SIMS methods for the detection of parts per billion (ppb) levels of U and Th in IC metallization and the sub-part per million (ppm) analysis of C, N and O in Si and GaAs materials. The reduction of both the radionuclide content in metallizations and the control of the C, N and O levels and distributions in Si and other semiconductor materials are central to the fabrication of reliable, high performance VLSI circuits.

The third approach for enhanced trace component analysis was the evaluation of evolving microanalytical techniques which provide these improved quantitation or detection limits. This evaluation resulted in the preparation of a detailed report describing and discussing the features of these new methods. As a result of this evaluation, three experimental investigations were initiated. These investigations included a preliminary study of accelerator-based SIMS, the design and initial fabrication of a time-of-flight (TOF) SIMS, and collaborative support of research for developing sub-micron liquid metal ion sources at the Oregon Graduate Center.

In addition, during the performance of this research, several additional analytical needs came to our attention. These included:

1. Improved depth profiling techniques which provide a more sensitive analysis of the outermost surface;

2. Improved depth resolution in the analysis of heterostructures and/or superlattice-type systems; and
3. The ever-increasing need for improved bulk analytical techniques which provide sensitivities and quantitative capabilities which meet the demands of the crystal-growth community and the users of semiconductor materials. The technologies requiring improved bulk analysis range from the existing silicon industry to III-V and II-VI semiconductors to the more advanced electro-optical materials utilized in infrared imaging (HgCdTe) and the photorefractive materials such as bismuth silicon oxide which is under investigation at the University of Southern California.

IMPLICATIONS FOR FURTHER RESEARCH

The results of this research program strongly suggest that two areas of research and development should be actively pursued in order to significantly enhance quantitative materials analysis capabilities. In the area of trace level analysis of microvolumes, this research has substantiated that secondary ion mass spectrometry techniques have the highest probability of successfully achieving sub-part per million (ppm) detection limits for a wide range of materials. In order to achieve this capability, however, two innovative approaches to SIMS analysis must be pursued. For trace level quantitation of materials with features having sub-micrometer dimensions this research strongly indicates that time-of-flight SIMS (TOF-SIMS) is the most viable approach. We envision that the successful development of a quantitative TOF-SIMS technique will occur in two stages. First, a prototype instrument which performs trace level analysis of rather large areas (~150 μm in diameter) should be developed. This instrument will utilize conventional reactive ion sputtering sources and will be very useful for trace level analysis of unknown impurities in sample-limited applications (e.g., very thin films, particles, etc.). Once this prototype instrument has been thoroughly evaluated with respect to both design and quantitative capabilities, a second generation instrument which incorporates post-sputtering ion enhancement and a sub-micrometer sputtering source should be developed. At this time, the most viable post-sputtering ion enhancement technique is nonresonant multiphoton ionization (MPI) which is accomplished with a pulsed, high power density laser system. Calculations performed in this research indicate that with commercially available Nd:YAG pulsed lasers, essentially all of the sputtered elemental species can be completely ionized by these lasers. The coupling of this near-unity ionization probability with a sub-micrometer liquid metal ion sputtering source should provide quantitative trace level microanalytical capabilities for most elements. Trace level quantitative analysis of

materials with device features greater than 10 μm can best be realized with the accelerator-based SIMS technique. Our research indicates that very substantial improvements in detection sensitivity over conventional SIMS analyses are achievable with this technique.

The second conclusion resulting from this research regards the most viable methods for enhancing quantitation in bulk analysis and improving depth resolution in large area depth profiling applications. Commercial instrumentation has recently been introduced which could possibly meet these analysis requirements. Glow discharge mass spectrometry (GDMS) is a new bulk analysis technique which promises to provide routine bulk analysis with part per billion (ppb) detection limits. A second technique, referred to as sputtered neutral mass spectrometry (SNMS), has the capability of performing quantitative depth profiles of large area samples with depth resolutions approaching 50 angstroms. Both these techniques produce the analytical signal primarily by ionizing the sputtered neutral species, and the elemental ion yields appear to be independent of the materials composition. As a result of this matrix-independent ion yield phenomena, quantitation of a given element in any matrix requires knowing only the ion yield of this element in one material standard. Thus, these techniques do not appear to require a suite of standards of different matrix composition for quantitative analysis. CHARLES EVANS & ASSOCIATES has recently purchased, with corporate funds, the first production instruments for both these techniques and we are actively pursuing the development of analytical methodologies for them.

REPORT

REPORT

I. Improving the Sensitivity and Quantitation of Existing Surface Analysis Techniques

During the first year of this program, we performed studies in three areas which resulted in either improved detection sensitivity or quantitation of existing state-of-the-art microanalytical techniques. The techniques utilized in this work were Rutherford backscattering spectrometry (RBS), wet chemical analysis, electron probe microanalysis (EPMA), scanning Auger microscopy (SAM), and secondary ion mass spectrometry/ion microanalysis (SIMS). The three areas studied included the following and are discussed in detail below:

1. Develop methods for improved quantitation of the microanalytical techniques of SAM and SIMS;
2. Evaluate methods for increasing the detection sensitivity of secondary ion mass spectrometry in the microanalysis of 10 to 150 micrometer diameter areas; and
3. Evaluate and develop methods for extending quantitative SIMS ion microanalysis down to smaller lateral dimensions.

A. Improvements in the Quantitative Depth Profiling Capabilities of SAM and SIMS

Although both the SAM and SIMS techniques are routinely utilized in the qualitative elemental analysis of a wide range of materials systems, quantitative analysis by these techniques requires the development and analysis of microanalytical standards which have a composition very similar to that of the unknown sample. These standards are required because the analytical signal for a given element produced by these techniques depends on the materials' overall composition. For example, in the SIMS analysis of equivalent Si concentrations in two different materials, e.g., Al and GaAs, the detected Si ion intensity is significantly different. In a similar manner, the SIMS ion yields for equal concentrations of different elements in the same matrix (e.g., B and Fe in Si) are generally quite different. These phenomena are referred to as matrix effects in SIMS analysis and, although these effects are well-documented, quantitative SIMS analysis can only be performed after the determination of the ion yield of element X in matrix Y

has been evaluated from a suitable standard. Similar matrix effects exist in scanning Auger microscopy. Thus, quantitative analysis by either technique requires standard materials and these standards must have a composition which is homogeneous on the scale of the analytical volume. As a result of this homogeneity requirement, both the high performance SAM and SIMS technique require standards which are uniform on the scale of micrometer dimensions.

Impurity and trace level component standards can be prepared as SIMS standards by using ion implantation techniques. The preparation and analysis of these types of standards is now a fairly routine procedure and has resulted in the development of a wide range of SIMS quantitative methodologies. Microanalytical standards preparation by ion implantation techniques is, however, practically feasible only for implant concentrations less than a few atomic percent. Another and equally important analytical requirement is the quantitative microanalysis of major and minor components in different materials systems and our research on quantitative SAM and SIMS analyses has focused on developing methodologies for this concentration regime. The approach we utilized in this research was the following:

1. Prepare thin film materials as potential standards;
2. Determine the bulk composition of the major and minor constituents in these "standards" with techniques that provide quantitative analysis at these concentration levels;
3. Analyze these standards by SAM and SIMS to insure concentration homogeneity on the microanalytical scale; and
4. Develop quantitative analytical procedures for SAM and SIMS from these analyses.

This protocol should provide a general method for the preparation and microanalytical characterization of the major and minor constituents for diverse materials systems. Once these analytical procedures are developed for large area analysis, they can be applied to the quantitative analysis of highly defined geometries in actual devices.

Two investigations were performed in this quantitative analysis program. The first study was to determine the quantitative capabilities of SAM and SIMS in the analysis of boron and phosphorus in borophosphosilicate glasses (BPSG). These glasses are extensively used in the semiconductor industry as intermetal dielectrics, surface passivation and encapsulant layers. The phosphorus in these glasses provides trapping sites for alkali metals and thus reduces the penetration of these elements into sensitive device regions, while the boron

reduces the glass reflow temperature to temperatures below 1000°C which are compatible with maintaining device integrity during glass deposition and processing. The concentration and in-depth distribution of these elements in the glass are very important parameters in device performance and reliability. For example, although the phosphorus is necessary for ionic gettering, it is also very detrimental if it comes in contact with the Al metallization in the device. Before the development of the quantitative SIMS in-depth analytical procedures which are described in detail in Appendix A, the most widely used analytical techniques for B and P analysis in BPSG were wet chemical (spectrophotometry) and electron probe microanalysis (EPMA). Although these techniques can quantitatively analyze these elements at the major and minor constituent level, they do not readily provide lateral or in-depth distribution analysis. Thin films of phosphosilicate (PSG) and BPSG glasses having different P and B concentrations were prepared on Si substrates for this study and the bulk composition of these glasses were determined by wet chemical, EPMA and RBS analysis. These samples were then analyzed by SIMS and SAM. It was readily apparent from the onset of these analyses that the Auger microprobe could not provide a useful analysis of these glasses because of the serious sample charging problems which occurred during electron bombardment of these insulating materials. In a similar manner, severe sample charging was observed in the initial SIMS analyses of these materials; however, the use of a sample voltage offset technique along with flooding the sample surface with an electron beam significantly reduced the extent of this charging effect. These analytical methods enabled us to obtain reproducible, quantitative analyses of the in-depth distributions of B and P in these glasses and this SIMS technique is now routinely utilized for the characterization of this highly relevant materials technology.

This detailed study of the BPSG compositional analysis illustrates the capabilities of deploying a microanalytical technique such as SIMS in the quantitative in-depth analysis of major and minor constituent levels. This capability, of course, depends on the preparation and quantitative characterization of standard samples by auxiliary techniques. We are presently evaluating the use of SIMS and SAM for the quantitative analysis of metal silicide films. These films have been quantitatively characterized at the major and minor constituent level by Rutherford backscattering spectrometry and the SIMS and Auger analysis of these technologically important films are in progress. We fully anticipate the successful development of quantitative microanalytical methods for these systems by SIMS and SAM.

B. Improvements in Secondary Ion Yields

The second area of investigation in this research determined the extent to which improvements in the quantitative detection sensitivity of secondary ion microanalysis could be achieved in the analysis of materials having lateral dimensions ranging from 10 to 150 micrometers. Improvements in the detection sensitivity of any analytical technique can be accomplished either by increasing the analytical signal or reducing the background noise. These processes increase the signal-to-noise (S/N) ratio which results in improved detection limits. In secondary ion mass spectrometry, the analytical signal can be increased by either increasing the secondary ion yield at the sample surface or by increasing the transmission of these ions from the sample to the detector. It is our conclusion that a significant increase in secondary ion transmission efficiency can be achieved by developing the TOF-SIMS technique and this subject is discussed in more detail in Section II of this report. In this section of the report, we present the results of our investigations on enhancing the ion yield of sputtered elements, while in the next section, processes which reduce the background noise in SIMS analyses are discussed. We present in these two sections the conclusions pertaining to S/N enhancement achievable with existing SIMS instrumentation. There are a variety of evolving techniques (such as TOF-SIMS) which may produce either significant signal enhancement or background reduction. These techniques are discussed in detail in the Section II and Appendix C of this report.

In the reactive ion sputtering process utilized in high performance SIMS analysis, both charged and neutral atomic and molecular (cluster) species are formed. As a consequence, an increase in the secondary ion signal intensity can be accomplished either by developing techniques which increase the ion yield in the sputtering process itself or by devising methods which efficiently ionize the neutral atomic species produced during sputtering. The development of reactive ion sputtering techniques is a successful example of how increasing the sputtered ion yield can significantly enhance the detection sensitivity of the SIMS technique. In the early development of the SIMS technique, researchers discovered that oxygen primary ion bombardment increased the ion yields of electropositive elements by orders of magnitude compared to the yields produced using inert gas ion (Ar^+) bombardment (1). Cs ion bombardment exhibited a similar enhancement in electronegative element analysis (2). One might assume that further ion yield enhancements could be achieved by utilizing a primary ion beam composed of a more electronegative element than O or a more electropositive element than Cs. Researchers have attempted to use a fluorine ion beam for electropositive element analysis in SIMS, but unfortunately, the highly reactive fluorine ions and neutrals emanating from this beam rapidly attacked the instrument components (lens,

apertures and insulators) (3). Thus, although ion yield enhancement could possibly be achieved with a F ion beam, the instrument itself would rapidly deteriorate and eventually be rendered useless. Since Cs is the most electropositive known (ionization potential = 3.893 eV), it is very unlikely that negative ion yields can be increased by using another elemental ion. As a consequence of these considerations, we strongly believe that secondary ion signal enhancements must come from techniques which ionize the neutral species produced in the sputtering process.

There are several possible methods to ionize these neutral components. These methods will be referred to as post-sputter ionization (PSI) techniques and include the following:

1. Electron impact (EI) ionization;
2. Laser ionization (LI); and
3. RF or DC plasma ionization (PI).

The plasma ionization techniques are an integral part of the recently introduced glow discharge and sputtered neutral mass spectrometry techniques which are discussed in Section II and Appendix C of this report. Although electron impact ionization of sputtered neutrals at first glance appears to be a simple approach for ion signal enhancement, it has been demonstrated that EI increases the secondary ion yield only a few per cent above that attainable with reactive ion bombardment. The major problem with this mode of ionization is that very large electron beam densities ($>10^4$ A/cm²) are needed to completely ionize the sputtered neutral species. Even if these high e-beam current densities were achievable without significant space-charge beam spreading, the electric fields set up by this current would severely distort the secondary ion extraction fields in a SIMS instrument.

The ionization of sputtered neutral species by high power laser irradiation appears to be the most viable approach for significantly increasing the ion yields in conventional SIMS analysis. There are two possible modes of ionizing sputtered elemental species by laser irradiation and these are referred to as resonant and non-resonant ionization. Resonant ionization can occur through the absorption of one or more photons of laser light, while nonresonant ionization requires multiple photon absorption and is commonly referred to as non-resonant multiphoton ionization (MPI). Single photon resonant ionization occurs when the energy of the laser photon is equal to or greater than the ionization potential (IP) of the atom such that the absorption of a photon by the atom produces the positive elemental ion and a free electron. Multiple photon resonant ionization occurs when several

photons are absorbed by discrete electronic energy states of the atom and the outermost electron in the atom is essentially promoted up through these levels to the ionization continuum. In nonresonant MPI, the very intense electromagnetic field generated by high power density laser irradiation creates "virtual" spectroscopic states through which the outermost electron is promoted to the ionization continuum (4).

Conceptually, single or multiphoton resonant ionization processes would appear to be the best method for ionizing sputtered elemental species since the ionization cross section for these processes are generally much higher than those of nonresonant MPI and one could envision selectively ionizing a specific neutral by "tuning" the output wavelength of the laser system (5). However, with state-of-the-art commercial laser systems, the elements which can be readily ionized in a single resonance process are the alkalis, Ca, Sr, Ba, Y, La, Al, Ga, In and Tl. (This estimate is based on utilizing a pulsed eximer laser operating at 193 nm (6.42 eV) and assuming that the single photon absorption cross section for these atoms are $> 10^{-20} \text{ cm}^2$.) It is also important to note that the reactive ion SIMS detection limits for these elements are already in the sub-ppm regime. Multiple photon resonant ionization techniques are very difficult to implement experimentally and do not appear suitable for high efficiency ionization of such elements as Fe, Zn, Cd or Hg which exhibit low secondary ion yields.

Since the technique of nonresonant multiphoton ionization does not require state specific laser wavelengths, it can, in principle, instantaneously ionize all of the neutral species sputtered from the sample material. However, high ionization efficiencies for nonresonant MPI require very large photon irradiances ($> 10^{23} \text{ photons/cm}^2\text{-sec}$) which are only achievable using pulsed laser systems. Since the duty cycle of these laser systems is very low (e.g., commercial high power Nd:YAG lasers produce 5 nsec pulses at a repetition rate of 10 Hz), these pulsed laser systems are not compatible with the continuous sputtering conditions utilized in conventional SIMS analyses. It is worth noting, however, that pulsed laser sources are very compatible with the pulsed primary ion beam utilized in TOF-SIMS, and post-sputter laser ionization techniques should provide significant detection sensitivity enhancement for this instrument (see Section II). The conclusion we reached from these considerations is the following. Although non-resonant multiphoton ionization has more general application for enhancing the extent of ionization of sputtered neutrals than does the resonant ionization process, neither technique can provide significant ion enhancement in conventional SIMS analyses because the laser source must operate in a pulsed mode (low duty cycle) in order to achieve the necessary large photon irradiances.

To this point in this discussion of post-sputtered ionization techniques, we have been discussing the ionization of neutral atoms which are in the ground electronic state. It is well known, however, that many sputtered neutrals are in electronically excited states. In fact, the technique referred to as SCANIIR is based on observing and quantitating the optical emission produced from these electronically excited sputtered neutral species (6). Since it might well be possible to ionize these excited species using a CW laser system (e.g., argon ion laser), we reviewed our SIMS analytical data in order to determine what neutral element or elements might be formed in excited states during the sputtering. The most obvious candidate appeared to be Hg sputtered from HgCdTe. In our DARPA research program dedicated to developing analytical methodologies for this material, we observed that the peak in the ion kinetic energy distribution for the sputtered Hg^+ was below the kinetic energy value the ion would have if it were formed in the near surface region above the sample. The sample potential on the IMS-3f ion microanalyser is held at +4.5 kV for positive secondary ion analysis, and this anomalous low energy peak in the kinetic energy distribution for the Hg cation was observed during ion energy scans of the secondary ions. The maximum Hg^+ ion intensity was observed to be below 4.5 keV which indicated either that most of the Hg^+ is formed by a gas phase collision process or possibly by electron ejection from an excited Hg neutral which has an excitation energy above the ionization potential (IP) of the neutral. The possible collision processes which could form the Hg ion include electron impact ionization and collisions of the neutral Hg with the incoming primary ions. It is also highly probable that the neutral Hg atoms are formed in electronically excited states since these collisional ionization processes would require very large cross sections in order to explain the high yields of the low energy Hg ions.

We postulated that electronically excited Hg atoms could be ionized using a 4 watt CW Ar ion laser (principle photon energy = 2.41 eV) and we modified the IMS-3f so that the output from this laser system traversed a section approximately 1 mm wide above the surface of the HgCdTe sample. The analysis consisted of scanning the kinetic energy acceptance window of the mass spectrometer over a large energy range as a function of the laser output power. We did not, however, observe any significant enhancement in the Hg ion intensity in the laser experiment. These negative results prompted us to fully evaluate the role of the incident primary beam in collisional ionization of the sputtered neutral Hg. This research was funded by the aforementioned DARPA contract and we concluded from these experiments that most of the Hg ions are, in fact, formed in collisions of the neutral Hg with the primary ion beam.

C. Reduction of Molecular Ion Interferences

As was mentioned in the introduction to the previous section, the S/N ratio obtainable in conventional SIMS microanalysis can be increased by reducing the background signal level. This background signal or "noise" in SIMS is produced primarily by molecular ion interferences. Several common molecular ion interferences which currently limit SIMS detection sensitivity include:

1. ^{30}SiH interference in the analysis of ^{31}P in Si;
2. $^{29}\text{Si}^{30}\text{SiO}$ interference in the analysis of ^{75}As in Si;
3. CO and N_2 interferences in the analysis of ^{28}Si in GaAs; and
4. ^{114}CdH interference in the analysis of ^{115}In in CdTe or HgCdTe

Although all of these spectral interferences can be eliminated by operating the SIMS instrumentation in either a high mass resolution (HMR) or sample voltage offset mode, these modes of operation reduce the transmission efficiency of the instrument which, of course, decreases detection sensitivity. Thus, the objective of this phase of our research was to evaluate methods for reducing or eliminating specific spectral interferences while at the same time maintaining a relatively high transmission efficiency for the secondary ion of interest. The two possible schemes we envisioned for reducing the intensity of these interferences were:

1. Laser dissociation or laser photodetachment of the molecular ion interferences; or
2. An accelerator-based SIMS technique.

The laser induced destruction of molecular ion interferences can be achieved through three different mechanisms:

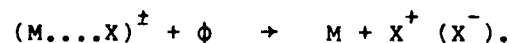
1. Laser photodetachment of negative molecular ions



2. Laser induced dissociation



3. Laser induced predissociation



The symbol (ϕ) in these processes represents the photon irradiance (photons/cm²-sec). The difference between laser dissociation and predissociation is a subtle one and relates to the time scale of the laser-molecular ion interaction. If the laser photons promote the molecular ion into a dissociating state during the ion formation, this process is referred to as laser predissociation. In order for these laser induced processes to be of practical value in conventional SIMS, it is necessary that a CW laser system be utilized for molecular ion destruction. The most likely candidate laser for these experiments is the CW Ar ion laser which can operate either in single line mode at wavelengths of 488 or 514.5 nm or in a multimode operation at wavelengths ranging from 514.5 through 476.5 nm. The photon energy produced by this laser is approximately 2.4 eV which should be sufficient to photodetach electrons from most negative ions in a single photon absorption process. The photodissociation of molecular ion complexes could, however, require multiple photon absorption if the bonding energy of these complexes is greater than 2.4 eV.

There are two configurations for laser irradiation of the sputtered material in the IMS-3f instrument. In the transverse mode, the laser light is directed slightly above the sample surface and the laser/sputtered material interaction volume is quite small ($\sim 1 \times 10^{-6} \text{ cm}^3$). In the longitudinal or normal mode of laser irradiation, the laser light is directed along the secondary ion flight path between the sample source and the electrostatic energy analyzer (ESA) of the instrument. The interaction volume in this mode of operation is $\sim .02 \text{ cm}^3$ because the ion flight path is approximately 1.0 M long. The much larger interaction volume in this mode of irradiation increases the probability of photodetachment or photodissociation by approximately 20,000 times over transverse illumination. Since the photodetachment or single photon photoionization cross sections can be very small ($\leq 10^{-19} \text{ cm}^2$) (7) and since our initial efforts at photoionization of sputtered Hg with transverse illumination were unsuccessful, we decided to implement the longitudinal mode laser irradiation scheme for these molecular ion interference studies.

In order to bring the laser along the ion flight path, we designed a special ESA and commissioned Cameca Instruments to fabricate this analyzer. This ESA had a hole through the outer sections of the analyzer so that the input laser beam passed through this hole and onto the ion flight axis. Unfortunately, this special electrostatic analyzer was found to distort the secondary ion focusing properties of the IMS-3f to such an extent that relatively routine analyses could not be performed. We expended considerable effort to correct the aberrations produced by this ESA, but were not able to achieve routine, reliable operation of this component. As a consequence, we did no further

research on laser-assisted spectral interference reduction, but rather concentrated our efforts in this area on the accelerator-based SIMS technique.

The accelerator-based SIMS (AB-SIMS), which is also referred to as "ultra-sensitive SIMS," concept was developed by Drs. Kenneth Purser, Theodore Litherland and Henry Gove (8). This technique is based upon the formation of negative secondary ions which are accelerated to very high kinetic energies (one to several Megavolts, MeV) and are passed through a stripper gas or stripper foil. The passage of these energetic negative secondary ions through this gas or foil strips one or more electrons from the ion and completely dissociates any molecular ion component in the incident ion beam. The positive ions produced from the electron stripping process along with the positive ions formed by molecular dissociation are accelerated out of this collision region and are subsequently energy and mass analyzed.

An instrument design for this type of analysis has been installed at the Department of Geology at the University of Toronto, Toronto, Canada. Mr. R. J. Blattner, J. C. Huneke and M. D. Strathman from our laboratory performed an experimental evaluation of this technique at the University of Toronto. A full discussion of the AB-SIMS technique and the results obtained in our preliminary evaluation of this technique are contained in Appendix B. The data can be summarized by stating the extrapolated detection sensitivities for B, As and Sb in Si obtained with this technique are on the order of ten parts per trillion atomic (ppta). As a consequence of these excellent detection sensitivities, we strongly believe that an AB-SIMS instrument dedicated to the bulk trace analysis of semiconductor materials would significantly benefit the advanced materials research community.

D. Focused Efforts to Improve Trace Component Detection Limits

One general conclusion that was apparent to us from the research discussed in the two preceding sections is that large improvements in the overall performance of materials analysis techniques may require completely new instrumental design concepts (e.g., AB-SIMS). The lack of success in our efforts to achieve orders of magnitude improvement in signal to noise ratios with the laser irradiation schemes discussed above motivated us to investigate methods which might significantly improve the achievable detection limits of specific analytical problems by "refining" the analytical methodologies. Significantly better detection limits were achieved in two specific analyses using this approach. These analyses are discussed in detail below and include :

1. The analysis of U and Th in Al and metal silicide materials utilized as interconnect metals in VLSI/MOS memories; and
2. The analysis of "atmospheric" impurities (e.g., C, N, and O) in Si and GaAs.

1. The Analysis of U and Th in Metallization

During the development of the 64k RAM several years ago, it was observed that trace levels of U and Th in the lead sealing glass used to package the ceramic DIP packages could produce errors in the operation of the device. These single event or "soft" errors were apparently caused by the deposition of significant amounts of energy in the device by alpha particles produced during the spontaneous decay of these radionuclides. These errors were eliminated by incorporating material in the die well which absorbed the energy of these energetic alpha particles. The concern over soft error production in the more dense 256k and 1M RAM chips has recently focused on the purity of the aluminum and metal silicides interconnect metals with respect to radionuclide content. Since these metals reside on top of the device itself, an intervening energy absorbing layer cannot be utilized to reduce the effects of the radionuclide decomposition products. In addition, since the features for these more dense devices are significantly smaller than those of the 64k RAM, the impurity levels for U and Th contamination in these metals have been set at 3 ppb or lower by the semiconductor industry.

When we were first approached concerning what existing materials analysis technique or techniques could achieve such detection limits, we concluded that reactive ion SIMS was the only readily available technique which might possibly achieve these detection limits. However, we initially felt that molecular spectral interferences, especially those which could be formed in the heavy metal silicide materials (e.g., MoSi_2 or WSi_2), could pose serious difficulties at the low intensity signal levels produced from ppb concentrations of U or Th. In addition, in order to demonstrate reliable SIMS analyses of these low levels of U and Th, it would be necessary to develop analytical methods which would provide reproducible SIMS data for higher concentration U and Th samples. This was necessary so that the SIMS concentration data would corroborate that obtainable by other bulk analysis methods (e.g., spark source mass spectrometry) for these higher concentration samples. During the analysis of several metals containing ppm concentrations of U and Th, we were able to significantly reduce the intensity of mass spectral interferences by utilizing large sample voltage offsets and/or high mass resolution analysis. As a consequence of these technique developments,

we have demonstrated 70 parts per trillion (ppt) detection limits for U in Al. In addition, the large variation in the results of several SIMS analyses of low levels of U and Th in metals has been shown to result from U and Th segregation as microprecipitates in the host metal. This precipitation phenomena was discovered by employing SIMS ion imaging/digital image processing (DIP) techniques. These digital image processing techniques were developed under the auspices of a HgCdTe contract sponsored by DARPA. The successful analysis of the "average" U and Th content in interconnect metals was also accomplished by utilizing long signal integration times (i.e., large sampling depths), so that the intensity fluctuations arising from these microprecipitates were, in effect, averaged out. Thus, a representative bulk analysis was produced from this microanalytical SIMS technique. The need to analyze a large number of interconnect metal samples for low level U and Th content is not practical by this SIMS technique because of the long analysis times. The recent availability of glow discharge mass spectrometry (GDMS) has the promise of solving this sample throughput problem and we will soon transfer this materials characterization to the GDMS technique. Although the ion useful yield (i.e., number of ions detected per atom sputtered) is lower in GDMS than it is in SIMS, the larger sampling rates of the glow discharge technique compared to SIMS should enable it to successfully perform this trace component analysis reliably and rapidly.

2. Improved Analysis of Atmospheric Impurities C, N and O

The control of the concentration and distribution of C, N and O in semiconductor materials is very important for several reasons. Trace levels of carbon in Si materials can act as nucleation sites for SiO_x precipitation and can dramatically affect the mechanical properties of the Si starting wafer (9). Similarly, oxygen precipitates in Si can serve as gettering sites for impurities unintentionally incorporated into the device during fabrication (10). C, N and O may be electrically active in GaAs materials and research suggests that O can form complexes with dopants introduced into this material (11). Since these three elements are ubiquitous in the various stages of device fabrication, they are referred to as "atmospheric" impurities. The trace level analysis for these elements is complicated by the fact that C, N and O are present at relatively high densities in the ultrahigh vacuum environment of most materials analysis instruments. Thus, the vacuum environment of the measuring technique may contribute a significant background signal for these components which raises the ultimate detection limits. As a result of these background levels, the C, N and O detection limits in both Si and GaAs by high performance SIMS analysis have for several years been relatively high. Since the demand for improved detection limits of these

elements has been increasing, we have focused our efforts in reducing the background signal levels. We found that by increasing the pumping speed in the sample chamber of the IMS-3f as well as in the primary ion beam column, along with sample pre-baking and sputtering impurity gettering material before the analysis, we have been able to significantly improve the C, N and O detection limits. The following table lists the current detection limits for these elements in Si and GaAs along with the best previous detection limits achievable in Si.

Detection Limits (ppma)

<u>Element</u>	<u>Si</u>		<u>GaAs</u>
	<u>1984</u>	<u>1983</u>	<u>1984</u>
C	<0.1	2	0.02
N	<0.01	0.1	0.2
O	<0.1	4	0.02

These excellent detection limits have been achieved with a relatively straightforward analytical approach and provide the semiconductor industry with a sensitive, rapid and reliable method of determining C, N and O levels in various Si and GaAs starting materials.

II. Investigation of Evolving Microanalytical Techniques

The future demands for trace level sensitivity in advanced electronic devices require surface microanalysis capabilities which can not be achieved by present day SIMS/ion microanalysis. The fundamental limitations of the SIMS technique are illustrated by examining the requirements of ppm detection sensitivities at a 0.1 micrometer lateral resolution and a 100 angstrom depth resolution. The total number of atoms contained in this microvolume is approximately 4×10^6 , so that even an optimized SIMS analysis having a useful yield of .05 (50% ionization efficiency and 10% transmission efficiency) would not produce a single count for a trace component at a 1 ppm concentration. It is apparent from this calculation that in order to achieve a detectable signal at this concentration in this volume of material, it is necessary to achieve ionization and mass analysis transmission efficiencies which approach 100%. Thus, we are lead to the conclusion that new analytical techniques must be developed and evaluated if the sensitivity and detection limits required for future device geometries are to be achieved.

Of equal importance was our finding during the present study of new microanalytical techniques that before one could approach the lateral microanalysis of 0.1 μm device geometries, significant improvements must be made in the capabilities of current bulk and depth profiling analyses. In our discussions with materials scientists, device engineers and crystal growth researchers, the following three key analytical requirements were often mentioned.

1. The continuing need in present semiconductor technologies, particularly those using Si, for more sensitive, surface specific analyses which identify and quantitate a breadth of surface contaminants produced during surface preparation and cleaning procedures.
2. The need for depth profiling techniques which have higher depth resolution. These improved depth profiling capabilities are required for a host of silicon technologies and for devices being fabricated from III-V and II-VI compound semiconductors. All of these requirements relate to devices which utilize very thin layers, or incorporate superlattice structures to provide the necessary electrical performance.
3. There is also a need for more sensitive analysis at the bulk impurity level. Silicon crystal growth technology is still plagued by the introduction of unintentional impurities during the growth process. Similar inadvertent impurity introduction commonly occurs in the growth of GaAs, InP, CdTe and HgCdTe materials. Newer materials which are highly insulating pose very difficult problems for sensitive, bulk analytical techniques, and these materials also require trace element analyses at concentration levels which range from 1000 to 0.1 ppm.

In our opinion, research in improved detection sensitivity can be broken down into two studies. The first area would focus on the achievement of improved in-depth and bulk analysis capabilities at lateral resolution between 0.1 mm to 1 mm. The second area would focus on improving the overall efficiency of signal generation and collection in order to achieve trace component analysis at sub-micrometer lateral resolutions. As a result of these two motivating factors, we investigated several evolving techniques which promise to provide improvements in depth resolution, bulk detection limits, and which could lead to low concentration level microanalysis of sub-micron features.

A report discussing these evolving techniques was prepared and submitted to DARPA. This report contains a brief introduction to each of these techniques followed by a short discussion of their relative advantages and disadvantages. The report concludes with a discussion of the relative analytical merit of

each technique along with an evaluation of the anticipated benefits further technique research would bring to the characterization of current and future materials and/or device technologies. This report is included as Appendix C.

As a consequence of the observations and conclusions of this report, we initiated several research projects in these areas within our organization. One of the most promising of the evolving techniques is accelerator-based SIMS. A significant amount of our research efforts was focused on planning, performing and evaluating the collaborative experiments performed at the University of Toronto. These results are summarized in the previous section and a full discussion of these very significant results are contained in Appendix B.

Another result of our evaluation of evolving techniques motivated us to initiate the design and construction of a time-of-flight SIMS (TOF-SIMS) system. Although this research represents a significant change in our original research objectives on this contract, we strongly believe that there are several materials and technology needs that would be best met by such an instrument. Since the strengths of a TOF-SIMS instrument are:

1. Its ability to simultaneously detect all the different mass ions produced from a given volume of material; and
2. The possibility of achieving very high ion formation, transmission and collection efficiencies,

such an instrument is ideal for the identification and quantitation of unknown contaminants contained in small volumes of material. In addition, the development of a sensitive TOF-SIMS technique equipped with a sub-micrometer diameter sputter ion source (e.g., liquid metal ion gun) could provide the lateral resolution and sensitivity capabilities required for trace component analysis of 0.1 μm device features. As a consequence, we have designed a TOF secondary ion mass spectrometer which can characterize impurities in inorganic or semiconductor materials.

We envisioned two phases in the development of this instrument. The first phase would concentrate on the design and evaluation of the ion optics using a relatively large diameter ($\sim 150 \mu\text{m}$) pulsed, sputter ion source followed by the incorporation of a sub-micrometer liquid metal ion gun in the second phase. During the ion optic design phase, we consulted with Professor Alfred Benninghoven of the University of Muenster in West Germany. Professor Benninghoven has designed a fully operational TOF-SIMS instrument which is utilized primarily for the analysis of high molecular weight organic molecules (e.g., amino acids, peptides and oligonucleotides) (12). We began an

experimental collaboration with Prof. Benninghoven although we realized that there were significant differences between a TOF-SIMS instrument dedicated to inorganic analysis and one developed for organic analysis. The primary difference in the two instruments is that inorganic technique will utilize a high kinetic energy, high current density reactive ion sputtering source which will impart a significant kinetic energy to the secondary ions. High efficiency collection of these energetic secondary ions requires ion optical elements not incorporated in Prof. Benninghoven's instrument. Secondly, the detection dynamic range must be much greater on an instrument for inorganic materials than one for organic materials analysis. We did attempt to perform elemental analysis on the TOF-SIMS instrument in Muenster, but could not obtain reliable SIMS data. We attribute this lack of success primarily to the fact that the Muenster instrument utilizes a rare gas (Ar) ion source and, hence, the secondary ion yields were orders of magnitude lower than those achievable with an O_2 or Cs reactive ion sputtering source.

Since we initiated this TOF-SIMS development in the latter part of the performance period of this current research contract, we have not completed the assembly or testing of this instrument. We have, however, submitted a proposal to continue this important development work. It is worth mentioning that we discussed this TOF-SIMS concept with a number of researchers in the semiconductor industry during the recent International SIMS Conference held in October, 1985 in Washington, D.C. These personnel strongly endorsed the need for a technique which could identify unknown impurities contained in very thin films or within sub-micrometer diameter areas.

The second phase of this TOF-SIMS development will evaluate the capabilities of a sub-micrometer beam diameter reactive ion sputtering source for achieving sensitive, high lateral analysis of small device features. The combination of this small diameter sputter source (which will most probably be a liquid metal ion source) with the high transmission efficiency of TOF mass spectrometry should provide routine sub-micrometer materials characterization capabilities. Since the liquid metal ion source concept appears to be the most fruitful approach to achieving a reliable, sub-micrometer diameter ion beam, we have funded research in this area through a subcontract of the current research program. This subcontract funded the support of a graduate student at the Oregon Graduate Center working under the direction of Professor J. Orloff. This research centered on developing a reliable, high current density, small beam diameter Ga^+ source and investigating various applications of this device. The report in Appendix D summarizes the results of this research. This research achieved Ga^+ beam diameters ranging from 0.3 to 0.5 μm at current densities ranging from 0.1 to 0.5 A/cm^2 . Part per million SIMS detection sensitivities should be attainable at this current density if the

sputter rate and ionization efficiency of Ga is similar to that of O_2 . (Or alternatively, one might flood the sample with O_2 during the analysis.) If further research on the TOF-SIMS technique is funded, we propose to continue this liquid metal ion source development and in particular, will explore methods of pulsing the beam on and off as well as investigate a Cs^+ source design.

III. Summary and Conclusions

In summary, we feel that this two and a half year research effort has been quite successful. We have been able to develop a variety of incremental improvements in existing techniques which have achieved improved quantitation and detection limits and have successfully applied these improved methods in novel applications. We have also investigated several more speculative areas, such as the low power density photoionization of potential metastable species, without much success. We feel that the study of accelerator-based SIMS and the initial development of a TOF secondary ion mass spectrometer have been quite rewarding and are the correct approaches to follow in future materials characterization research. A proposal will be submitted for developing an accelerator-based SIMS to be utilized in research for DARPA and DoD and we hope to continue the TOF-SIMS development under the auspices of a renewal contract which will be administered by AFTAC at Patrick AFB in Florida. The topic of nonresonant multiphoton ionization has been pursued by other workers and does seem to have some applicability as we proceed into a new generation of semiconductor materials. The potential usefulness of MPI processes in materials analysis will be incorporated into the prospective TOF-SIMS research program we have proposed.

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APPENDIX A

Quantitative Determination of Boron and Phosphorus in
Borophosphosilicate Glass by
Secondary Ion Mass Spectrometry

by

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Analytical Chemistry, 1985, 57, 1071.

Quantitative Determination of Boron and Phosphorus in Borophosphosilicate Glass by Secondary Ion Mass Spectrometry

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Secondary ion mass spectrometry (SIMS) using positive oxygen ion bombardment and positive secondary ion spectrometry was applied to the quantitative depth profile analysis of insulating borophosphosilicate glass (BPSG) films. The sample charging problem was alleviated by prior deposition of a thin gold layer onto the samples, use of an electron flood gun, and automatic sample voltage optimization. The SIMS results were compared to data acquired by wet chemical analysis and Rutherford backscattering (RBS), and excellent quantitative correspondence was obtained. The wet chemical analysis results were then used to calibrate the SIMS results quantitatively. In addition to the SIMS analytical procedures, the advantages of SIMS over conventional analytical techniques such as electron microprobe, wet chemical methods, and Auger electron spectroscopy are also discussed.

Phosphosilicate glasses (PSG) and borophosphosilicate glasses (BPSG) have found important applications in silicon semiconductor devices as the intermetal dielectric between aluminum metalization and polysilicon or refractory metal silicide interconnects as well as a surface passivant and encapsulant layer (1, 2). There are several advantages of PSG and BPSG over undoped SiO_2 glasses. Phosphorus acts to provide trapping sites for alkali metals and thus minimizes impurity penetration into sensitive devices (3). Further, since microelectronic circuit manufacturing has recently adopted processing procedures operating below 1000 °C in order to minimize unintentional dopant diffusion, the reflow temperature of glasses can be reduced by increasing the P content (4-6). However, it is well-known that a substantial increase in the phosphorus content in particular next to the Al metalization can lead to corrosion of the aluminum runs, unstable film composition, and reliability problems (7-10). There is thus a practical upper limit of approximately 8-9 wt % of P in these films before these undesirable effects occur. It is also known that the addition of B to the glass serves to further lower the reflow temperature to a device-compatible range of significantly under 1000 °C. Unfortunately, B has no abilities at gettering ionic contaminants.

The boron and phosphorus concentration and in-depth distribution in BPSG are very important parameters for the glasses utilized in electronic device technology. For instance, an increase in the B concentration lowers the stress, while the film etch rate in HF solutions is determined by the ratio of the boron to phosphorus concentrations in the BPSG's (11). Although these glasses have significant advantages in device manufacturing, the high porosity and hygroscopicity of the BPSG films permit moisture to penetrate into the glass and react with the phosphorus to form phosphoric acid. Should

this occur in close proximity with the underlying aluminum metalization, then corrosion of the aluminum runs by the phosphoric acid is highly probable. This is a significant cause of device failure in PSG or BPSG coated devices. Thus, the correct manufacturing process for deposition of these glasses not only must control the concentrations of the B and P but must also ensure that P is essentially depleted near the glass/metal interface, while B incorporation in this region provides the necessary suppression of the glass softening point.

To date, the most widely used analytical techniques for BPSG analysis have been electron microprobe analysis and wet chemical methods. These techniques are in general quite accurate, but do not provide information concerning the in-depth and lateral distribution of the B and P dopants. Moreover, the detection limit for B by electron microprobe analysis is not very good, usually about several atomic percent. Other analytical techniques less commonly used are Auger electron spectroscopy (AES), $^4\text{He}^{2+}$ Rutherford backscattering (RBS), and secondary ion mass spectrometry (SIMS). The principal drawbacks for AES analysis are that sample charging under electron bombardment and ion sputtering can sometimes be too severe to circumvent. Rutherford backscattering analyses provide accurate thickness measurement of the glass film and reasonably good dopant quantification but suffer from low phosphorus sensitivity because P is very close in mass to Si. The detection limit of P by RBS analysis is about 1%. The detection limit can be lowered if the BPSG films are thin (less than 5000 Å) and channeling techniques can be employed. The B sensitivity is very poor because of the dominant oxygen and silicon backscattering in the same energy range and the low B backscattering yield. Another drawback for electron microprobe and Rutherford backscattering analyses is that very little in-depth information is provided.

The SIMS technique is commonly used in the semiconductor field because of its high sensitivity and the capability to detect all the elements in the periodic table and to provide lateral and in-depth information. However, quantification of data obtained by SIMS is nontrivial because of the significant variation in secondary ion yields for different elements and for the same element in different materials (matrix effect). Bulk and ion implant standards are thus commonly used for quantification (12-14). Quantitative SIMS analysis of insulators is further hampered by sample charging under energetic ion bombardment. Negative oxygen ion bombardment is routinely used for insulators, especially in geological applications. However, the maximum attainable ion current and sputtering rate are about a factor of 50 less than that accomplishable by O_2^+ bombardment for the CAMECA IMS-3f, thus making O^- sputtering inappropriate for routine depth profiling. In this paper, an analytical methodology to circumvent this sample charging problem using O_2^+ bombardment is described,

and the applications of secondary ion mass spectrometry (SIMS) to the quantitative analysis of BPSG are discussed. SIMS results for the analysis of BPSG are compared to results obtained from electron microprobe, wet chemical, and Rutherford backscattering (RBS) analyses. Excellent quantitative correlation among the various analytical techniques is observed.

EXPERIMENTAL SECTION

Sample Preparation. The phosphosilicate glass (PSG) and borophosphosilicate glass (BPSG) films were deposited with a commercial Watkins-Johnson WJ-985 atmospheric pressure chemical vapor deposition (APCVD) equipment with three deposition stages. This instrumental setup allows fabrication of up to three BPSG films with various composition onto the same sample, requiring only one passage through the equipment (15, 16). The films were produced at 430 °C with silane, phosphine, and diborane making up approximately half a percent of the injectors' flows and oxygen approximately 30%. The balance was nitrogen. Atmospheric CVD characteristically produces more fully oxidized films. Films produced at reduced pressures, especially plasma induced, contain substantial phosphorus, for example, as P_2O_3 and PH_3 as well as P_2O_5 (17).

Wet Chemical Analysis. BPSG films to be analyzed for B were deposited on 4 in. diameter Si(100) wafers with a Si_3N_4 surface layer 1500 Å thick and stripped by a NaOH solution. BPSG films to be analyzed for P were deposited on bare Si(100) wafers and stripped by HF. The resulting solutions were analyzed by colorimetry employing a Sequoia-Turner spectrophotometer. Standards for P and B quantification were prepared from potassium dihydrogen phosphate and boric acid, respectively.

Electron Microprobe. The PSG samples were analyzed by using a CAMECA MBX electron microprobe relative to calibration standards of pure silicon and a phosphate mineral (apatite) with a known P content. The electron beam energy for X-ray excitation was 8 kV, and the k emission lines were analyzed. The total excitation depth was about 1 μm . These PSG films were specially made to be more than 2 μm thick in order to ensure that the excitation volume remained well within the PSG.

Rutherford Backscattering Spectrometry. Rutherford backscattering analysis was performed using a General Ionex Corp. Tandem Model 4110A. A $^4He^{2+}$ beam of approximately 2 mm in diameter was accelerated to 2.275 MeV and impacted the samples at roughly normal incidence. The samples were mounted on a graphite disk with carbon paste. The backscattered particles were detected by surface barrier detectors placed at 170° and 110°. Each energy spectrum was taken after a total of 20 μC of backscattered particles had been integrated. The P concentrations in the films were calculated by comparing the number of He particles backscattered by P in the BPSG films to those films to those backscattered from the Si atoms in the substrate. The ratio was then normalized by the inverse of the square of the respective atomic numbers to account for the variation in backscattering efficiency due to differences in the atomic nuclear backscattering cross section. The accuracy of this method is estimated to be about $\pm 5\%$.

Secondary Ion Mass Spectrometry. To minimize sample charging under oxygen ion bombardment, the following steps were adopted: (1) a gold layer of about 1000 Å was deposited on top of the PSG and BPSG samples using a Fullam sputtered gold coater; (2) these gold-coated samples were mounted in a multiple sample holder made of tantalum and stainless steel, and conductive silver paint was used to ensure good electrical contact between the holder and the sample surface; and (3) an electron flood gun was utilized during the analysis to compensate for the residual sample charging.

A CAMECA IMS-3f ion microanalyzer equipped with an oxygen duoplasmatron primary ion source was used. A primary oxygen beam composed of mainly O_2^+ was focused to about 50 μm in diameter and the ions were accelerated to 8 keV relative to the sample potential. The typical primary current was 3 μA and the primary beam was rastered over an area of 500 by 500 μm^2 . The secondary accelerating voltage was set at 4500 V and a Faraday cup was used as the detector. The IMS-3f was interfaced to an HP9825A microcomputer for instrument control, data acquisition,

and data reduction. One BPSG sample was analyzed by using the PHI 6000 secondary ion profiler equipped with a quadrupole mass analyzer.

RESULTS AND DISCUSSION

The most serious problem encountered during SIMS analysis of insulators in general and BPSG in particular is sample charging which can significantly degrade the SIMS analysis. The steps described in the above paragraph minimized electrical charging, but charging was not totally eliminated. Moreover, the degree of sample charging was not constant throughout the depth profile analysis. Sample charging was observed to be more severe at the beginning of the analysis and became progressively less pronounced as the sputtering front approached the underlying conducting Si substrate. Since it was impractical to change the electron gun current during the course of the depth profile, the secondary ion accelerating voltage was scanned under computer control to establish the optimal secondary ion accelerating voltage for each analysis cycle. Since this automatic technique required a reference mass, the ^{30}Si matrix ion was profiled simultaneously with B and P. In order to correct for any ion transmission variation due to changing sample charging states throughout the analysis, the B and P secondary ion intensities were normalized to the ^{30}Si secondary ion current in each cycle, assuming that any variation in ion transmission would affect the matrix (Si) and the impurity (B and P) ion signals to the same extent. There is a molecular ion mass interference by ^{30}SiH at mass 31, the nominal atomic mass of P, and a mass resolving power of about 3500 is required for separating the ^{31}P ion signal from the hydride mass interference to provide a trace elemental detection limit. While this resolving power is routinely attainable on the CAMECA IMS-3F, the application of this high mass resolution technique is very difficult in the present analysis which requires a reasonably high sputtering rate using O_2^+ bombardment on insulating samples. As a consequence, the measurements were made under low mass resolution conditions. The practical detection limit for P by SIMS analysis with the hydride mass interference unresolved is about 0.05 atomic percent. This detection limit for P is quite acceptable for BPSG analysis, as the concentration of interest is generally above 1 at. %. The detection limit of B is determined by the Faraday cup detector dc offset. A lower B detection limit (parts per billion) can be achieved by reducing the mass spectrometer ion transmission and detecting the decreased B ion current on an electron multiplier with pulse counting electronics.

Figure 1 illustrates a SIMS depth profile for B, P, and Si in a test Si wafer sample which has a 1 μm thick BPSG passivation layer. Note that there is a buffer region which contains no detectable P between the BPSG and the underlying Si. This buffer region is essential to the prevention of corrosion of the metalization in real electronic devices. Figure 1 also illustrates the extent of the actual secondary accelerating voltage adjustment (shown in the sample offset curve) required to obtain the maximum ion intensity for each analysis cycle. This curve thus reflects the variation in sample charging throughout the depth profile. It can be observed that sample charging is most severe in the near surface region and becomes progressively less pronounced during the course of the analysis. The detection limit of B and P is imposed by the Faraday cup dc offset and the hydride mass interference, respectively.

In order to evaluate the capability of SIMS to provide quantitative analyses, a set of PSG samples were analyzed by both electron probe microanalysis and SIMS, and the results obtained from the two techniques are compared to each other. A plot of the P concentrations (atomic percent) calculated from electron microprobe measurements vs. the $^{31}P/^{30}Si$ secondary ion intensity ratios obtained by SIMS is presented

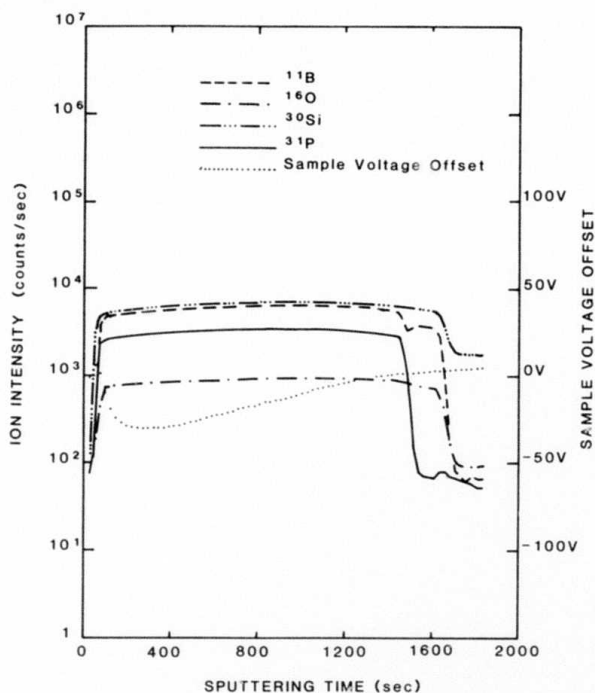


Figure 1. SIMS depth profile of B, P, O, and Si of a BPSG film.

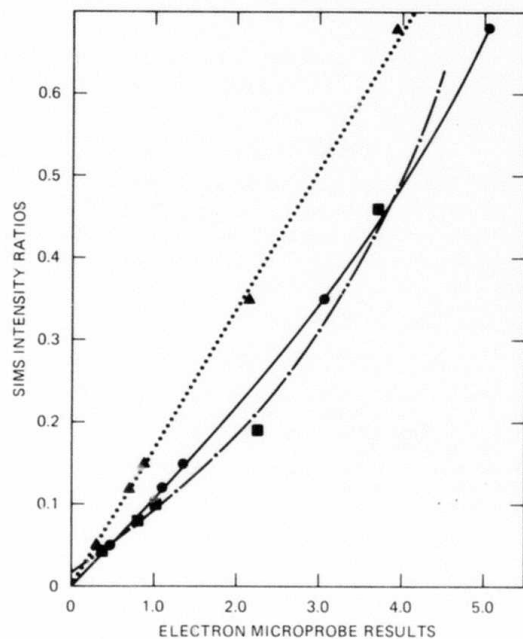


Figure 2. (●) SIMS P/Si secondary ion intensity ratios vs. electron microprobe P atomic percent. (▲) SIMS P/Si secondary ion intensity ratios vs. electron microprobe P/Si atomic percent ratios; (■) SIMS P/O secondary ion intensity ratios vs. electron microprobe P/O atomic percent ratios. Both ordinate and abscissa scales are arbitrary.

in Figure 2. Since the Si concentration varies with the P doping, the relationship is not linear. As a consequence of the variable matrix ion intensities for BPSG with different compositions, quantification schemes employing the use of ion implant standards are not very accurate because a constant matrix ion signal is usually assumed in the calculation. As shown in the same figure, good linearity is, however, observed if the SIMS ion intensity ratios of P to Si are plotted vs. the concentration ratios of P to Si acquired by the electron microprobe analysis. The use of ^{16}O as the normalization ref-

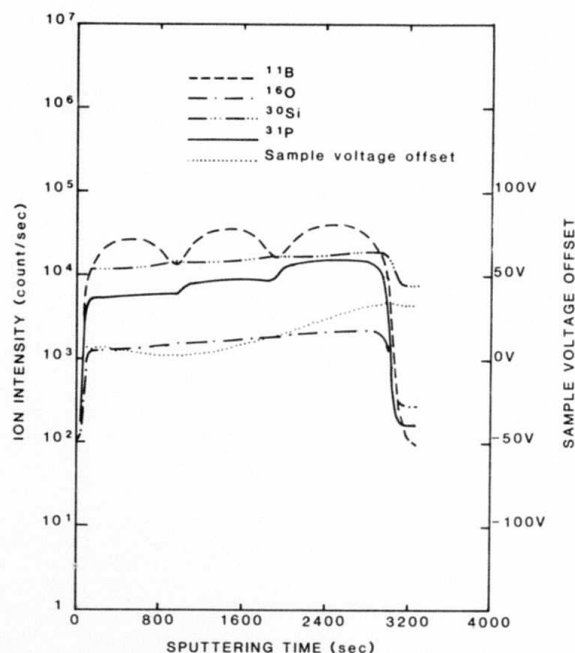


Figure 3. SIMS depth profile of B, P, O, and Si of an APCVD BPSG film with three composite layers.

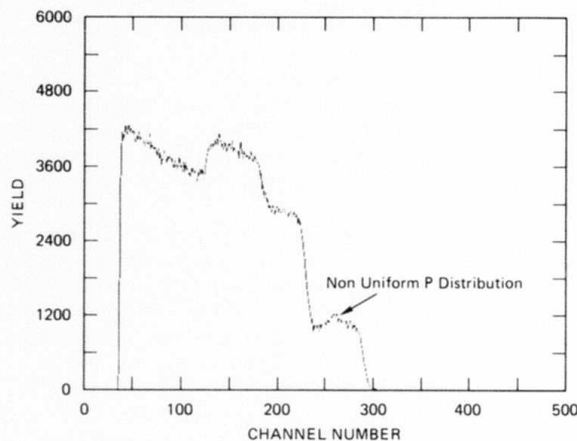


Figure 4. RBS spectrum of the sample with three composite BPSG layers.

erence is not appropriate, firstly, because under the present sputtering conditions, a significant fraction of the secondary oxygen ions are derived from the implanted primary oxygen ions, and, secondly, the secondary oxygen ion signal may depend on the vacuum. The poor linearity is demonstrated in the SIMS P/O ion intensity ratios vs. electron microprobe P/O concentration ratios plot shown in Figure 2.

The SIMS depth profile of one of the BPSG standards is exhibited in Figure 3. The in-depth distributions of B and P are observed to vary in these samples because these BPSG standards are a composite of three layers (individually adjustable). To confirm that the B and P variations in the BPSG film are real and not due to some instrumental artifacts, the sample was reanalyzed using a PHI 6000 secondary ion profiler. The results obtained are identical with those acquired on the CAMECA IMS-3F. In addition, as shown in Figure 4, the nonuniform in-depth distribution of P is clearly indicated in the RBS spectrum. Owing to these variations, the B, P, and Si ion intensity profiles must therefore be integrated over the total sputtered depth to obtain the total B and P concentrations in these BPSG films for comparison with the

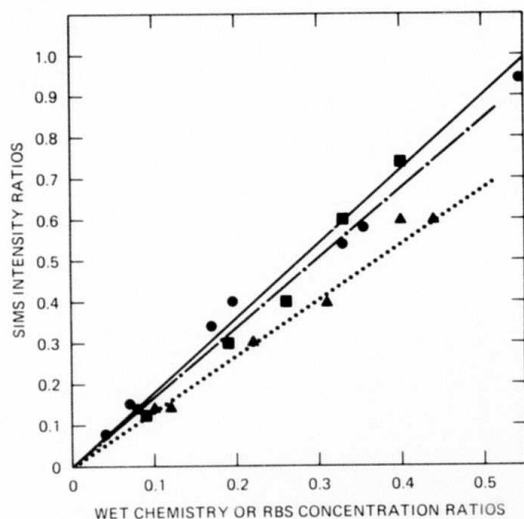


Figure 5. (●) SIMS B/Si secondary ion intensity ratios vs. colorimetry B/Si weight percent ratios. (▲) SIMS P/Si secondary ion intensity ratios vs. colorimetry P/Si weight percent ratios. (■) SIMS P/Si secondary ion intensity ratios vs. RBS P/Si atomic percent ratios.

bulk techniques employed for standardization.

The B and P contents in the rest of the films were also measured by wet analysis/colorimetry and Rutherford backscattering spectrometry. The P concentrations were calculated from the RBS backscattered particle energy spectra by comparing the amount of He particles backscattered by P in the BPSG films to those backscattered by the Si atoms in the substrate, with the assumption that the densities of the BPSG films and bulk Si are the same. The linearity obtained from SIMS ion intensity ratios vs. wet chemistry concentration ratios and against RBS concentration ratios is again seen to be good (Figure 5).

On the basis of the results generated from the electron microprobe analysis, wet chemical analysis, and Rutherford backscattering analysis, relative sensitivity factors can be derived to convert the SIMS B/Si and P/Si ion intensity ratios into B and P concentrations. Once these relative sensitivity factors are established, the SIMS technique can then be applied to the in-depth concentration analysis of B and P in other PSG and BPSG samples. Figure 6 depicts the depth profile of the BPSG sample shown in Figure 3 replotted on concentration vs. depth scales using the appropriate relative sensitivity factors derived from wet chemistry data.

The advantages of SIMS in this type of analyses are 4-fold: (1) the depth profiling capability is intrinsic to the sputtering process and therefore provides a direct measure of the in-depth elemental distribution, (2) the fast sputtering rate achievable using O_2^+ provides routine analysis capability in a process environment, (3) with the aid of empirical standards, quantification using SIMS can be accurate to within $\pm 15\%$, and (4) the high detection sensitivity of SIMS allows the detection of low concentrations of B as well as unintentional contaminants such as Na, K, and Cr in the glasses and the interfacial regions. Careful interpretation of the results is, however, necessary because of the high mobility of alkalis under an electric field.

In conclusion, the SIMS technique employing O_2^+ sputtering has been demonstrated to provide quantitative in-depth concentration profiles of B and P in PSG and BPSG films. Given appropriate cross-calibration, the same analytical methodology can be applied to other dielectric films such as

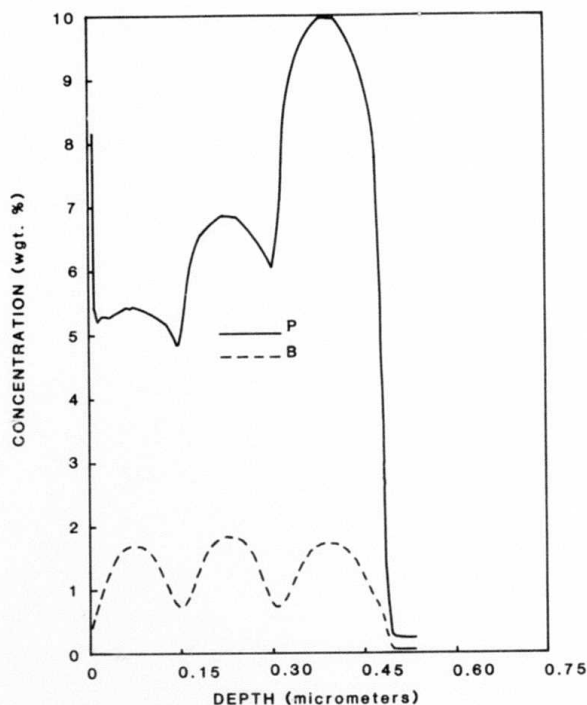


Figure 6. Quantitative replots of B and P profiles of the APCVD BPSG film with three composite layers.

CaF_2 or SrF_2 used for GaAs device passivation, ZnSe for HgCdTe device passivation, and other similar materials systems.

ACKNOWLEDGMENT

The authors wish to express sincere thanks to R. Fitzgerald for the electron microprobe analysis, S. Bauman for the Rutherford backscattering analysis, N. Gralenski for technical support, and M. Smith for his background work with a BPSG matrix.

Registry No. B, 7440-42-8; P, 7723-14-0.

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RECEIVED for review August 30, 1984. Accepted January 15, 1985. This work was supported in part by the Defense Advanced Research Projects Agency under Contract No. MDA 903-83-C-0099. This work is approved for public release and unlimited distribution. Review of the material does not imply DoD endorsement of factual accuracy and opinion.

APPENDIX B

Evaluation of Accelerator-Based Secondary Ion Mass Spectrometry
For the Ultra-Trace Elemental Characterization
Of Advanced Semiconductor Materials
Using the Isotrace Facility at the University of Toronto

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Abstract

In recent years, secondary ion mass spectrometry (SIMS) has made significant contributions to advanced semiconductor development in both the silicon and gallium arsenide technologies. The utility of SIMS in this context stems from the inherent sensitivity of the technique for analysis of trace-level impurities and dopants in either the bulk or depth profiling analysis modes. However, as impurity concentrations continue to decrease due to improvements in crystal growth and materials preparation, conventional SIMS detection limits have tended to become inadequate when addressing contemporary analytical needs. For a number of technologically important elements, these limitations arise from the presence of molecular ion spectral interferences, quite common in conventional SIMS.

An analogous situation existed some years ago in the field of ^{14}C dating metrology. Then existing techniques, including conventional mass spectrometry, were incapable of analyzing very old artifact specimens with sufficient sensitivity to produce an accurate age. Mass spectrometric measurements of ^{14}C were found to be limited by molecular ion interferences much like present-day SIMS analysis of semiconductor materials. Researchers at the University of Rochester in the late 1970's found that dramatically improved detection limits for ^{14}C could be achieved in a SIMS-like measurement employing an MeV tandem ion accelerator. The advantage gained by working at high energy in a tandem accelerator is that molecular ions are dissociated in the charge stripper canal, a standard component in any such system. Thus it was found that species such as $^{12}\text{C}^{1}\text{H}$, $^{13}\text{C}^{1}\text{H}$ and other spurious molecular ions which ordinarily interfere with ^{14}C could be effectively eliminated without the customary concomitant loss in analyte signal (detection limits).

Two facilities have since been established in North America for ^{14}C dating based on the accelerator SIMS concept, one at the University of Arizona and the other at the University of Toronto. Although these instruments are optimized for ^{14}C analysis, the purpose of this study was to evaluate the potential of accelerator-based SIMS for ultra-trace impurity analysis of semiconductor materials as exemplified by boron, phosphorus, arsenic, antimony and iron impurities in silicon. Our results for arsenic and antimony suggest that detection limits in the 10^{-10} to 10^{-11} atm-cm $^{-3}$ range should be possible for these elements with only relatively minor alterations to existing instrumentation and operating protocols. Comparable sensitivity may be achieved for phosphorus in silicon, but a greater degree of instrumental refinement will be required. Boron, having a lower electron affinity than phosphorus, arsenic or antimony, was found to be somewhat less sensitive as expected. (Forming a negative ion of the analyte species of interest is a

prerequisite to "tandem" acceleration.) Iron in silicon proved to be an extreme example of this same fundamental problem that will require a different type of ion source than the one available to us for these experiments in order to achieve the desired level of sensitivity improvement.

The report that follows discusses:

1. The background and underlying principles of the accelerator-based SIMS technique as contrasted to conventional SIMS,
2. The application of accelerator-based SIMS to typical semiconductor analysis problems as represented by boron, phosphorus, arsenic, antimony, and iron in silicon,
3. An evaluation of currently available accelerator-based SIMS instrumentation, albeit optimized for ^{14}C analysis, and
4. Recommendations for possible future work.

I. Introduction and History

A. Conventional SIMS

During the past ten years, conventional secondary ion mass spectrometry (SIMS) has progressed from a laboratory curiosity to a widely accepted, routine analytical technique for trace-element, "surface" and microanalysis. Nowhere has the impact of this maturation been greater than in the advanced semiconductor technologies, most notably silicon (VLSI) and gallium arsenide, with both R/D and production applications. Numerous examples can be found in the context of bulk crystal growth (1-3), formation of epitaxial layers (4-7), ion implantation (8-11), process monitoring (12) and failure analysis (13). The main reason for the success of SIMS in dealing with these various problem areas stems from the inherent sensitivity of the technique when implemented in an optimized fashion (14). In this sense, optimization refers to the utilization of reactive primary ion bombardment (O_2^+ or Cs^+) for enhancement of ion yields of electropositive or electronegative elemental impurities, a high current density primary ion source to produce the greatest possible secondary ion flux and hence analytical signal from the specimen, the use of high extraction/transmission efficiency ion optics and mass spectrometer to effectively transport the secondary ions through the instrument, and a low noise ion-counting detection system. Also important to the implementation of high-performance SIMS are high mass resolution (up to $M/\Delta M = 10,000$),

secondary ion initial kinetic energy discrimination and a UHV sample chamber. These latter considerations are paramount when contending with the copious molecular ions prevalent in conventional SIMS mass spectra.

Detection limits in conventional SIMS are often adversely influenced by molecular ions arising from matrix components, primary ion beam species, residual vacuum constituents, impurities, or any of the above in combination. The Cameca IMS-3f ion microanalyzer, commercially available since 1978 and currently dominant in the high performance SIMS instrumentation marketplace, embodies all of the aforementioned capabilities for circumventing molecular ion interferences. Even with the advantages of the IMS-3f, conventional SIMS encounters fundamental detection limitations, in general, when viewed from a materials characterization perspective. Present analytical demands of the crystal grower, process engineer or materials scientist have essentially exceeded contemporary state-of-the-art trace-element analysis technology.

Table 1 lists IMS-3f detection limits for some of the more common dopants and impurities in silicon and gallium arsenide.

Table 1

Nominal IMS-3f Detection Limits (atm-cm^{-3})
For Selected Impurities in Silicon and Gallium Arsenide

Element	Si	GaAs	Bombarding Ion
B	3×10^{13}	2×10^{13}	O_2^+
As	1×10^{15} (ED)	---	Cs^+
P	3×10^{15} (HMR)	not measured	Cs^+
Sb	2×10^{13} (ED)	not measured	Cs^+
Fe	1×10^{16} (HMR)	1×10^{15} (ED)	O_2^+
Si	---	2×10^{14} (ED)	Cs^+
Na	1×10^{12}	1×10^{12}	O_2^+
Au	1×10^{12} (ED)	1×10^{13}	Cs^+
Se	not measured	1×10^{15}	Cs^+
Te	not measured	1×10^{13}	Cs^+

ED = Energy Discrimination

HMR = High Mass Resolution

Although the analysis of boron and sodium in silicon or selenium and tellurium in gallium arsenide are essentially interference-free, other analyses such as phosphorus or iron in silicon are severely inhibited by molecular ion backgrounds ($^{30}\text{Si}^1\text{H}^-$ at $^{31}\text{P}^-$ and $^{28}\text{Si}_2^+$ at $^{56}\text{Fe}^+$). Measures can be taken to discriminate against molecular ions (e.g., high mass resolution), but invariably these procedures lead to a loss in analytical signal (to gain in

signal-to-background), degrading detection limits from what they would be in the absence of the interference.

In conventional high performance SIMS, secondary ion accelerating potential is typically 1 to 10 kV, comparable to other forms of mass spectrometry. Secondary ion energy and the abundance of molecular ion interferences at the final detector are the quintessential differences between conventional SIMS and accelerator-based SIMS (AB/SIMS), the subject of this report.

B. General Principles of Accelerator-Based SIMS (AB/SIMS)

The primary hardware difference between conventional SIMS and AB/SIMS is the use of a high energy ion accelerator in the AB/SIMS system. There are two generic types of ion accelerators, single-ended machines and tandems. In a single ended machine the entire ion source "floats" at the accelerating potential (positive or negative) such that any ions formed with the same polarity as the source will be accelerated by the terminal voltage toward a ground plane and the target. Typical examples of these types of accelerators are ion implanters and Van de Graaffs. Alternatively, in a tandem accelerator, the ion source is biased slightly negative with respect to ground potential and is configured to produce negative ions either directly by Cs^+ ion beam sputtering or by charge exchange in a vapor cell containing a partial pressure of an electropositive element (e.g., lithium). Once produced, these negative ions are accelerated to a positively charged terminal at the center of the tandem where they are passed through a charge stripping canal containing a gas such as argon or a thin stripper foil. In the stripper, electrons are removed by collisional ionization forming positive ions in various charge states. These positive ions, formed by electron removal from the injected negative ions in the stripper cell, are accelerated away from the terminal to a second ground plane symmetrically situated with respect to the source and referred to as the "high energy end" (the ion source and injection optics being the "low energy end"). The tandem accelerator configuration yields an effective multiplication of the terminal voltage vis-a-vis final particle energy.

If a molecular ion is produced at the source and accelerated into the stripper cell, multiple electron losses will occur, giving rise to the instantaneous existence of molecules in an elevated charge state (+2 or greater). In almost every case, multiply charged molecules will spontaneously decompose, presumably due to Coulomb repulsion. In this fashion, a molecular ion will be dissociated into its component atoms with a partitioning of energy from the precursor molecule based on simple kinematic considerations. In essence, it

is this opportunity for molecular ion dissociation in the charge stripper of the tandem accelerator that makes AB/SIMS advantageous compared to conventional SIMS.

C. Application of AB/SIMS to ^{14}C Dating

Purser, et al. at the University of Rochester (15) were the first to apply tandem accelerator technology to a SIMS-like analysis, viz. for the determination of ^{14}C in artifact samples (radiocarbon dating). Extraordinary means are required for this analysis because the concentrations of interest are almost always quite small ($< 5 \times 10^{10} \text{ atm-cm}^{-3}$). Radioactive carbon-14 (half life = 5730 years) is produced through spallation processes in the atmosphere induced by cosmic radiation. At equilibrium, the rate of production of the radioisotope is equal to the rate of loss through beta decay. The concentration of ^{14}C in living organic matter arising from normal biochemical processes and interactions with the natural "pool" of ^{14}C is about one part in 10^{12} . After death, ^{14}C ceases to be replenished in the material. Consequently the concentration of ^{14}C will decrease over time in a predictable manner. For contemporary samples in which there are some 10^{11} radioactive nuclei present, radioactivity attributable to ^{14}C is on the order of 15 disintegrations per minute. Counting techniques will not have particularly good sensitivity for dating purposes because of the long times required to accumulate a statistically meaningful signal unless large and/or highly preconcentrated specimens are analyzed. Dramatically improved sensitivity for ^{14}C would be achieved if total atom detection (say by mass spectrometry) could be performed.

Two basic problems are encountered when attempting to analyze ^{14}C by conventional mass spectrometric techniques. One arises from molecular ion interferences such as $^{12}\text{C}^{1}\text{H}_2$ and $^{13}\text{C}^{1}\text{H}$, which can be circumvented by high mass resolution ($M/\Delta M = 2,000$) at the expense of spectrometer transmission. The other problem is an isobaric interference from ^{14}N which is very constraining for high mass resolution ($M/\Delta M = 70,000$). The most successful recorded effort of this type of measurement has been by Anbar, et al. (16), but the results were ultimately limited by other unresolvable molecular ion interferences to about 1 part in 10^{11} ($5 \times 10^{11} \text{ atm-cm}^{-3}$) $^{14}\text{C}/^{12}\text{C}$. Purser and his co-workers found that molecular ions could be eliminated in a tandem accelerator by dissociation at the terminal stripper, while $^{14}\text{N}^-$ is not produced in the ion source during cesium ion sputtering because nitrogen has an electron affinity of zero. Thus, ^{14}C could be analyzed by AB/SIMS free of interferences to levels of < 1 part in 10^{15} ($5 \times 10^7 \text{ atm-cm}^{-3}$).

Since the early work at the University of Rochester, two General Ionex Corporation (GIC) tandem accelerator facilities have been established in North America for ^{14}C dating, one at the University of Toronto and one at the University of Arizona. Our experiments were performed using the Toronto machine because it was considered by Dr. Purser (Chief Scientist at GIC and designer of the two ^{14}C machines) to be the one best suited for survey semiconductor analyses of the type we proposed. In recent years, a number of specialized non- ^{14}C ultra-trace analytical measurements have been performed at the University of Toronto well beyond the purview of conventional methodologies. Some examples are ^{36}Cl in ground water (17), ^{53}Mn and ^{10}Be in Antarctic specimens (18), ^{129}I in meteorites (19) and natural Pt and Ir in geological samples (20). In some instances, specialized protocols are required for particular isotopes due to hardware restrictions imposed by the ^{14}C optimization of the equipment, but generally speaking, the only requirement for AB/SIMS to be effective is that the species of interest form a negative ion by Cs^+ ion sputtering with reasonable efficiency. Therefore the technique is well suited for those elements having a relatively high electron affinity such as carbon, oxygen, the halogens, n-dopants and noble metals, but is handicapped in analyzing elements with low electron affinities like cadmium, mercury, nitrogen, zinc, alkali metals and p-dopants. In a later section we will discuss ways of avoiding this restriction that have been employed at the Isotrace Laboratory (University of Toronto) for analysis of elements with unfavorable electron affinities, in particular ^{26}Al (21).

II. Accelerator-Based SIMS Instrumentation at the University of Toronto Isotrace Laboratory

Figure 1 shows the instrumental configuration of the AB/SIMS machine at the University of Toronto. The instrument consists of a sputtering ion source, magnetic analyzer, MeV ion accelerator, and high energy ion detection system. Overall the system is similar to a conventional negative ion SIMS instrument with a tandem accelerator inserted between the mass spectrometer and final detector.

The major mission of the Isotrace facility using this machine is the dating of archaeological samples. In addition to this primary mission, several additional tasks are included in the laboratory charter. Among these is the investigation of AB/SIMS as a general purpose, albeit unique, materials

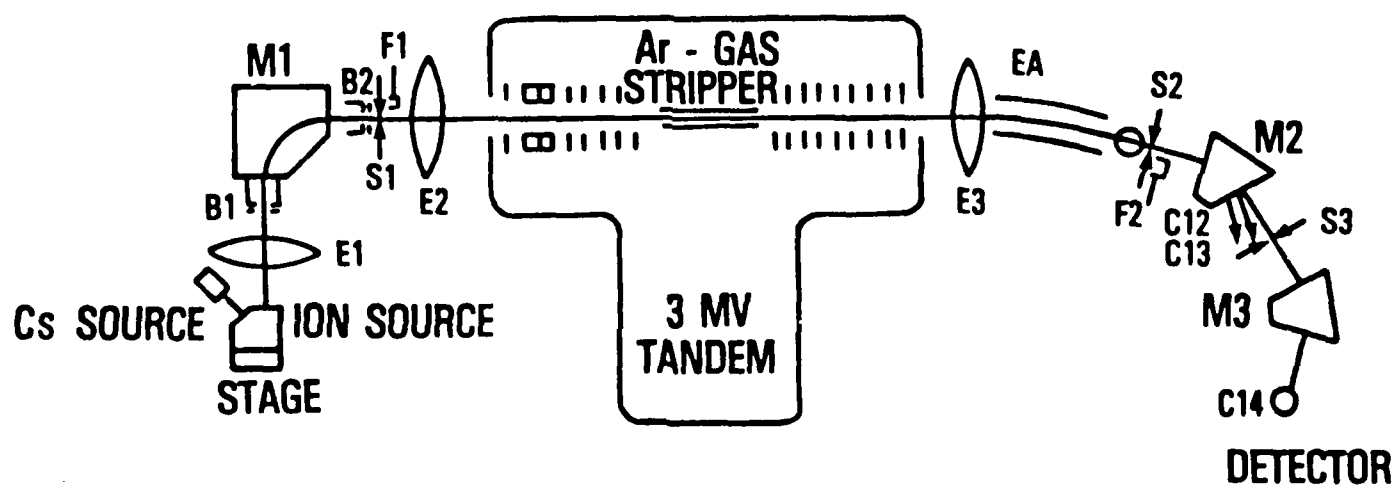


Fig.1

analysis tool. Because of this range of tasks assigned to the facility, the machine is configured in a reasonably general way but with an obvious emphasis on ^{14}C dating.

Figure 2 shows a cross sectional view of the sample introduction system and secondary ion extraction optics. The primary ion beam (A) is generated in a GIC SIMS II ion source with beam optics provided by a combination Einzel lens and electrostatic steering assembly situated between the ion source and the secondary ion extraction hemisphere (C). Positively charged cesium ions enter the grounded extraction hemisphere through a hole drilled at approximately 45 degrees from the sample normal. The sample is isolated from ground and held at a negative potential (typically -20kV) with respect to the extraction hemisphere. The sample is covered by a plate (D) which intercepts any stray Cs^+ beam, thereby serving as a final aperture. Secondary ions produced by the sputtering process are accelerated through a hole in the hemisphere normal to the sample surface and into the field free flight tube (B).

The secondary ion beam is focused by a gridded Einzel lens at E1 prior to entering an injection magnet (see Figure 1 for the references contained in this and the following paragraphs). The injection magnet (M1) serves as the low energy mass spectrometer for the system and is used to select the mass to be injected into the tandem for acceleration to MeV energies. The exit trajectory from the magnet is defined by a pair of adjustable slits (S1). Beam current measurements can be made behind these slits by inserting a Faraday cup into the ion optical path (F1). Final focusing prior to injection into the main accelerator is provided by a pair of gap lenses (B1 and B2) and a matching Einzel lens. The injected negative secondary ion beam is then accelerated to the positively charged terminal at the center of the tandem and into an argon gas stripper cell. The gas stripper converts the injected negative ions into positive ions and is a normal component of any tandem accelerator system. (For SIMS applications, the stripping process also serves the dual function of providing molecular ion dissociation.) Positive ions produced by the stripping process are accelerated away from the positively charged terminal to an exit ground plane. It should be noted that the transmission of the accelerator is near unity by virtue of a phenomenon referred to as "phase space compression." Spectrometer transmission in any ion optical system is often limited by angular divergence in velocity space. However, in a high energy accelerator, because the acceleration is axial and large, transverse velocity components will be relatively small, giving rise to a nearly paraxial beam. Transmission losses through the accelerator are thus negligible.

- A** Primary column, direction of incident beam.
- B** Secondary ion trajectory.
- C** Extraction hemisphere (ground).
- D** Aperture plate.
- E** Sample holder.

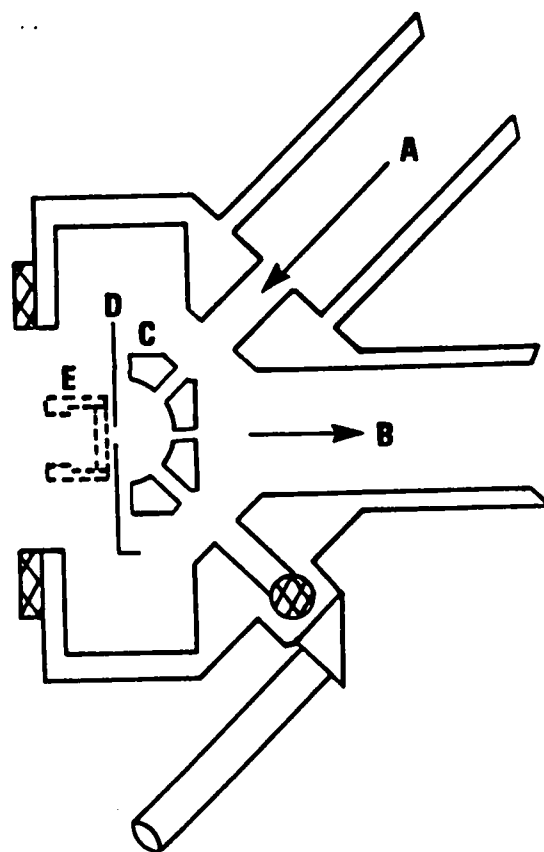


Fig.2

After exiting the accelerator, the beam traverses an electrostatic quadrupole (E3) before entering a 15 degree electrostatic analyzer (EA). The controls for E3 and EA are wired so that they can be varied in unison. This electrical configuration facilitates tuning beams with different "rigidities," defined in terms of the radius of curvature that will be followed by a charged particle traveling through any given magnetic field. Increasing the particle mass or energy will increase rigidity while increasing charge state decreases rigidity. This relationship was exploited in our measurements of arsenic and antimony as will be discussed in a later section.

After the ESA are a second set of slits (S2) and a second Faraday cup (F2). A typical beam spot size at the slits is approximately 1 mm. The first high energy magnet (M2) is located directly after F2 and is strong focusing. The magnet is designed to have a short focal length with isotopic dispersion in the exit focal plane (e.g., to separate ^{12}C , ^{13}C and ^{14}C). The magnet also has a "straight through" port for studies which do not require magnetic filtering of the high energy beam. Unfortunately, when the vacuum housing for this particular magnet was fabricated it was not properly aligned, leading to a permanent axial error of several degrees. This manufacturing defect requires that a small amount of fringing magnetic field be used to deflect any beam into the straight through beam line, subsequently configured with a beam stop and surface barrier detector.

The 45 degree exit line of M2 is equipped with two fixed Faraday cups located slightly in excess of the nominal 45 degree exit trajectory. These cups are positioned so as to intercept the less magnetically rigid ^{12}C and ^{13}C beams while allowing the heavier ^{14}C beam to continue along the normal beam line. There is a third set of slits at this point (S3), followed by a combination Faraday cup/surface barrier detector. The selection of detection device is accomplished by manually inserting either the Faraday cup or the surface barrier detector into the flight path. The final mass filtering device is a second strong focusing magnet (M3) used primarily for ^{14}C dating. At the exit of the second high energy magnet is a final surface barrier detector.

The detection electronics package used for these experiments consisted of a Keithley model 903 electrometer for all analog, direct current measurements (injected and transmitted beam), and a particle counting system comprised of:

1. Tennelec surface barrier detectors
2. Ortec detector bias supply
3. Tennelec model TC-170 preamplifier
4. Ortec model 572 shaping amplifier
5. Tennelec model TC-450 single channel analyzer
6. Ortec Lin/Log ratemeter
7. Tennelec model TC-812 pulser
8. Tennelec model TC-536 counter/timer
9. Canberra counter/timer
10. Nucleus model 1024D multichannel analyzer

Figure 3 shows a photograph of the Toronto AB/SIMS instrument as it was configured during our experiments. Clearly visible are the low energy end, control electronics chassis and part of the tandem accelerator including the high voltage power supply contained within the "T" leg. Figure 4 shows a better view of the ion source (Figure 4A) and a rear view of the low energy mass spectrometer and injection optics (Figure 4B). The high energy end, obscured in Figure 3, is shown in Figure 5. Figure 5A shows, from the left, the high energy end of the accelerator tank, quadrupole triplet lens, electrostatic analyzer, Faraday cup/particle detector assembly and the first high energy magnet immediately behind the gas cylinder regulator in the photograph. Figure 5B shows the second high energy magnet and final detector system. The "footprint" of the machine is approximately 60 feet from the ion source to the final detector and about 25 feet from the rear of the accelerator flight tube to the front face of the high voltage power supply.

One physical concept unique to a tandem accelerator that ultimately impacts AB/SIMS analysis should be emphasized. Any injected negative ion will be accelerated to the terminal potential just prior to arriving at the charge stripper. Because multiply charged negative ions are extremely rare, if they exist at all, the ion energy at this point will be equal to the terminal voltage in MeV. Collisional charge stripping in a gas cell is an inherently statistical process dependent upon such factors as cross section, gas pressure and path length through the cell. If the injected species is atomic, e.g., $^{28}\text{Si}^-$, the beam exiting the stripper cell will be composed of $^{28}\text{Si}^+$, $^{28}\text{Si}^{+2}$, $^{28}\text{Si}^{+3}$, . . . $^{28}\text{Si}^{+n}$. Each of these positive ions is formed in the stripper cell at a high positive potential; thus, the singly charged species will be accelerated a second time gaining an additional MeV of energy. A doubly charged positive ion will receive an additional energy of 2 MeV, the +3 charge

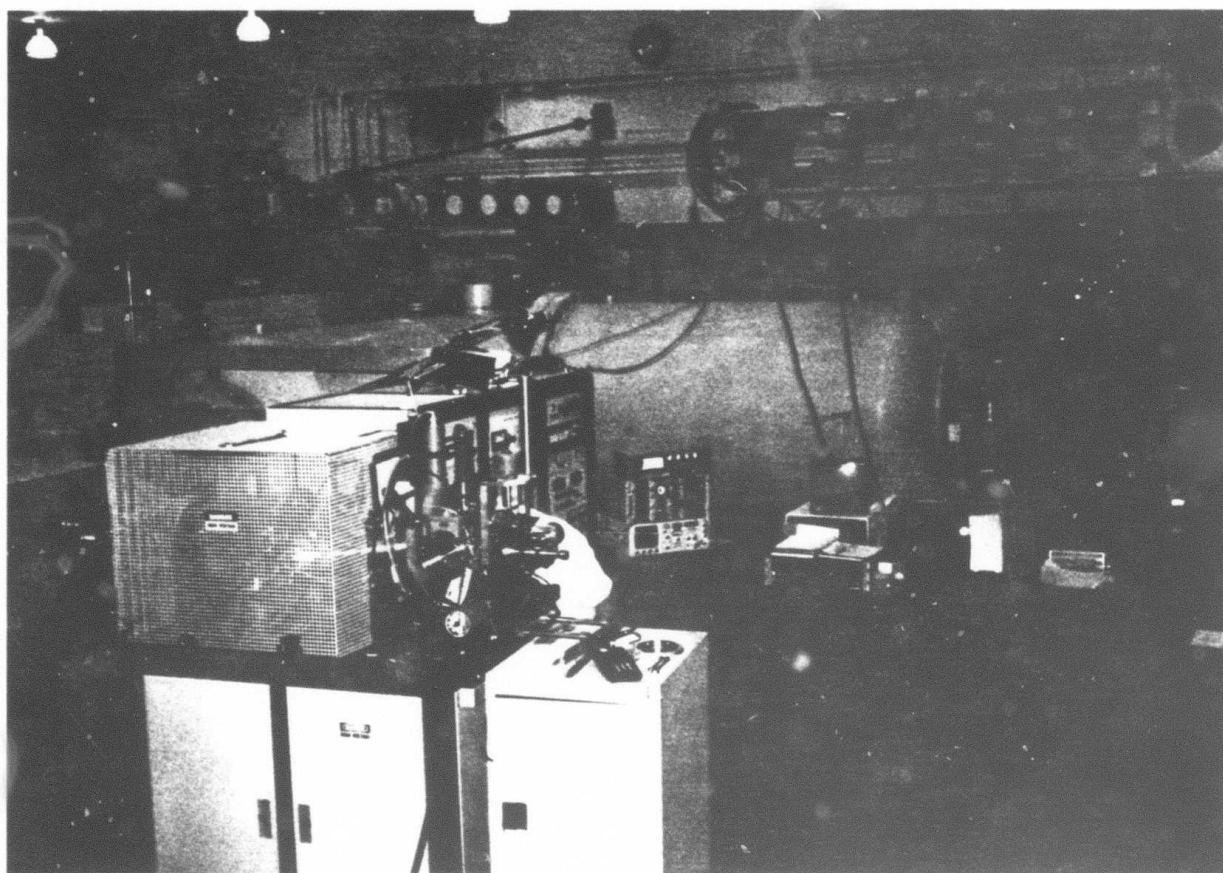


Fig.3

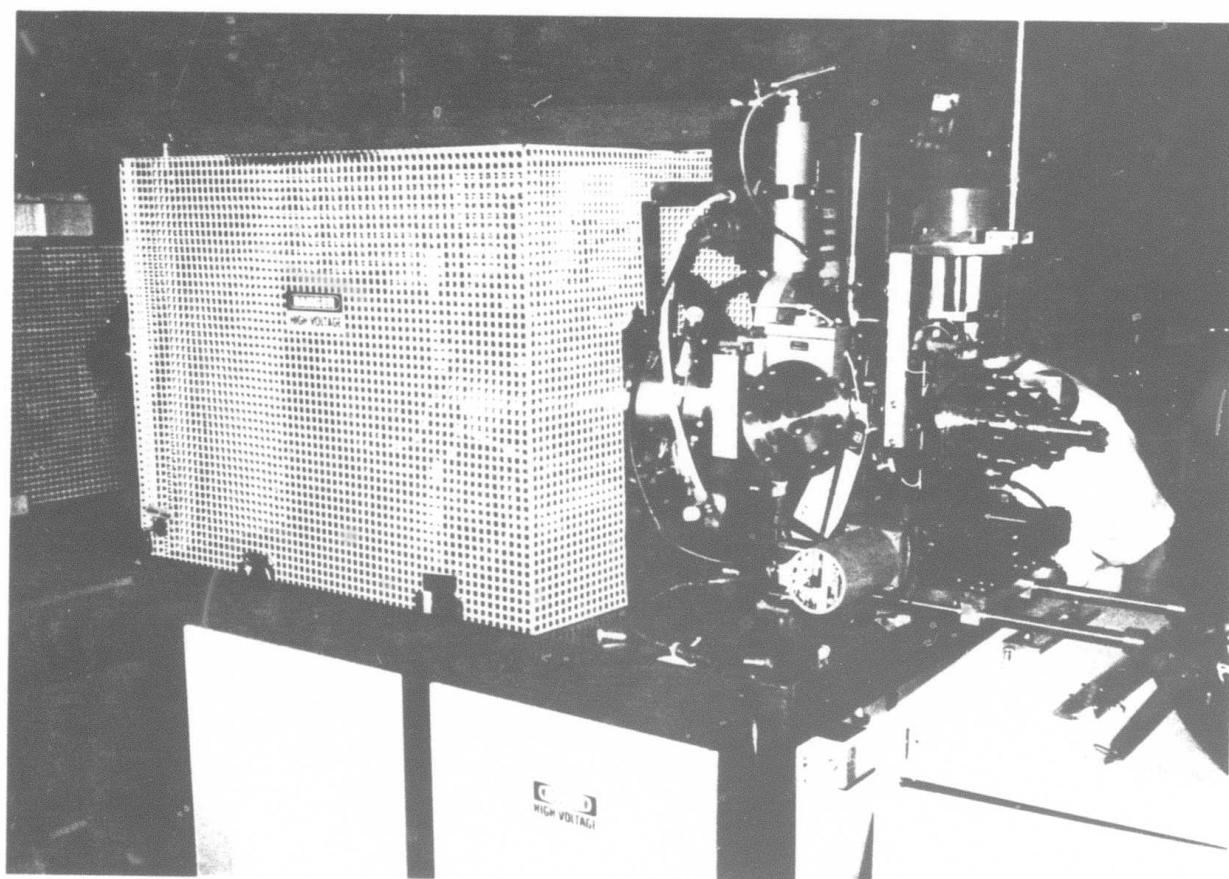


Fig.4 (a)

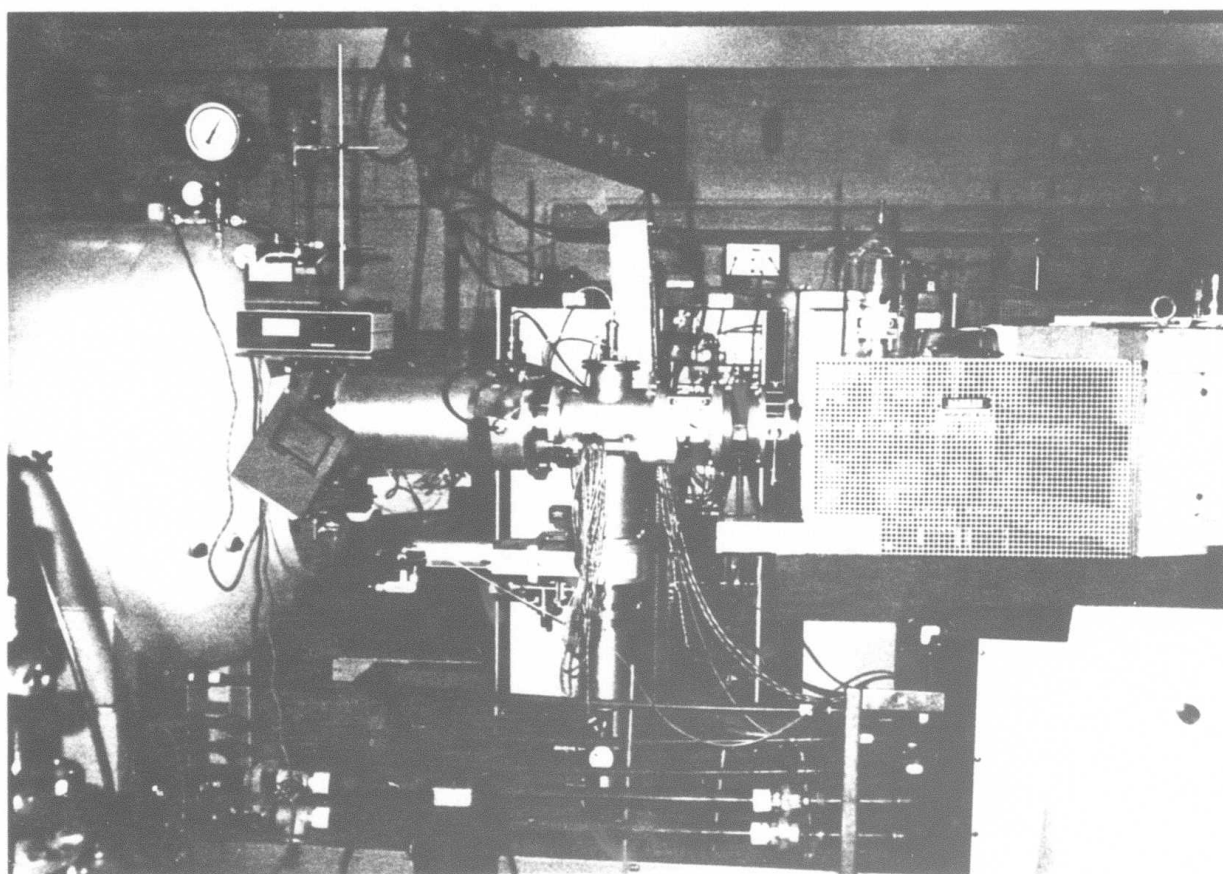


Fig.4 (b)

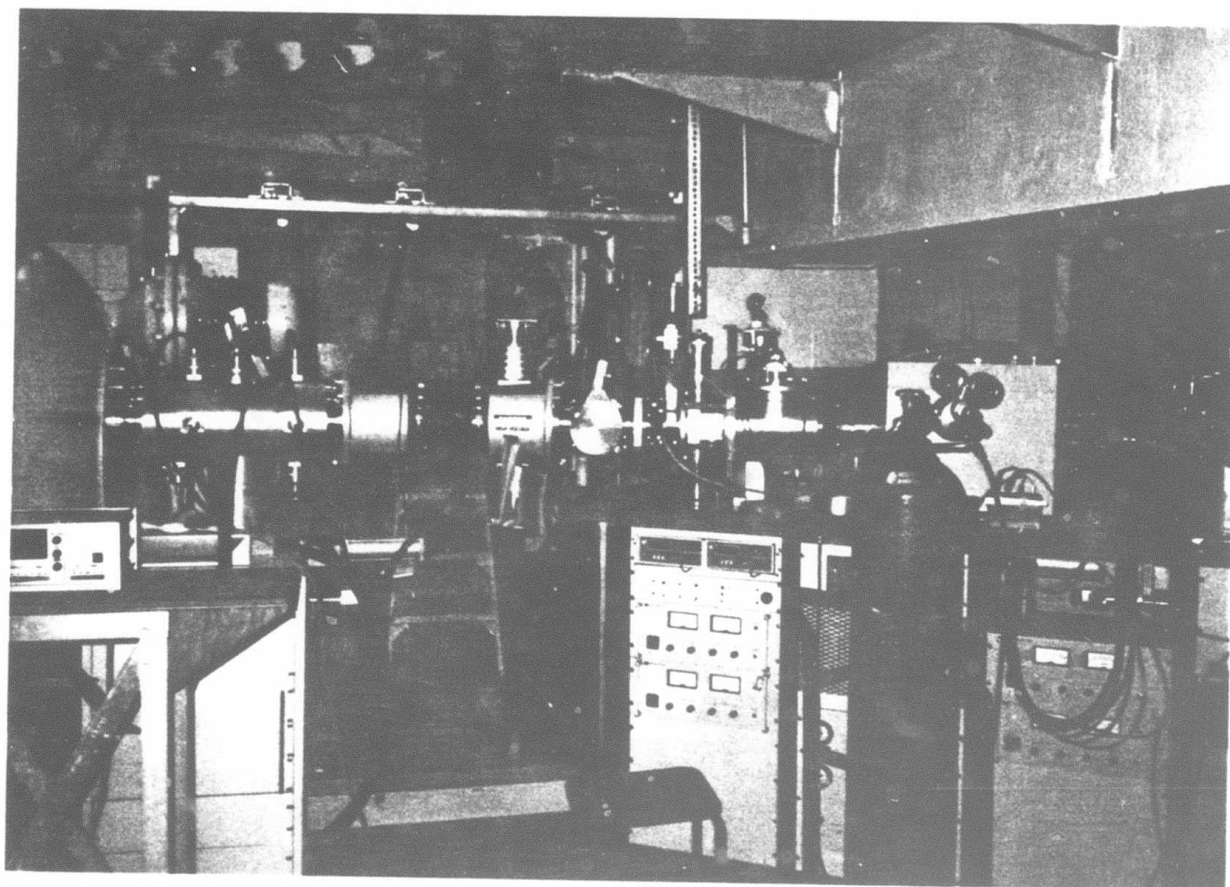


Fig.5 (a)

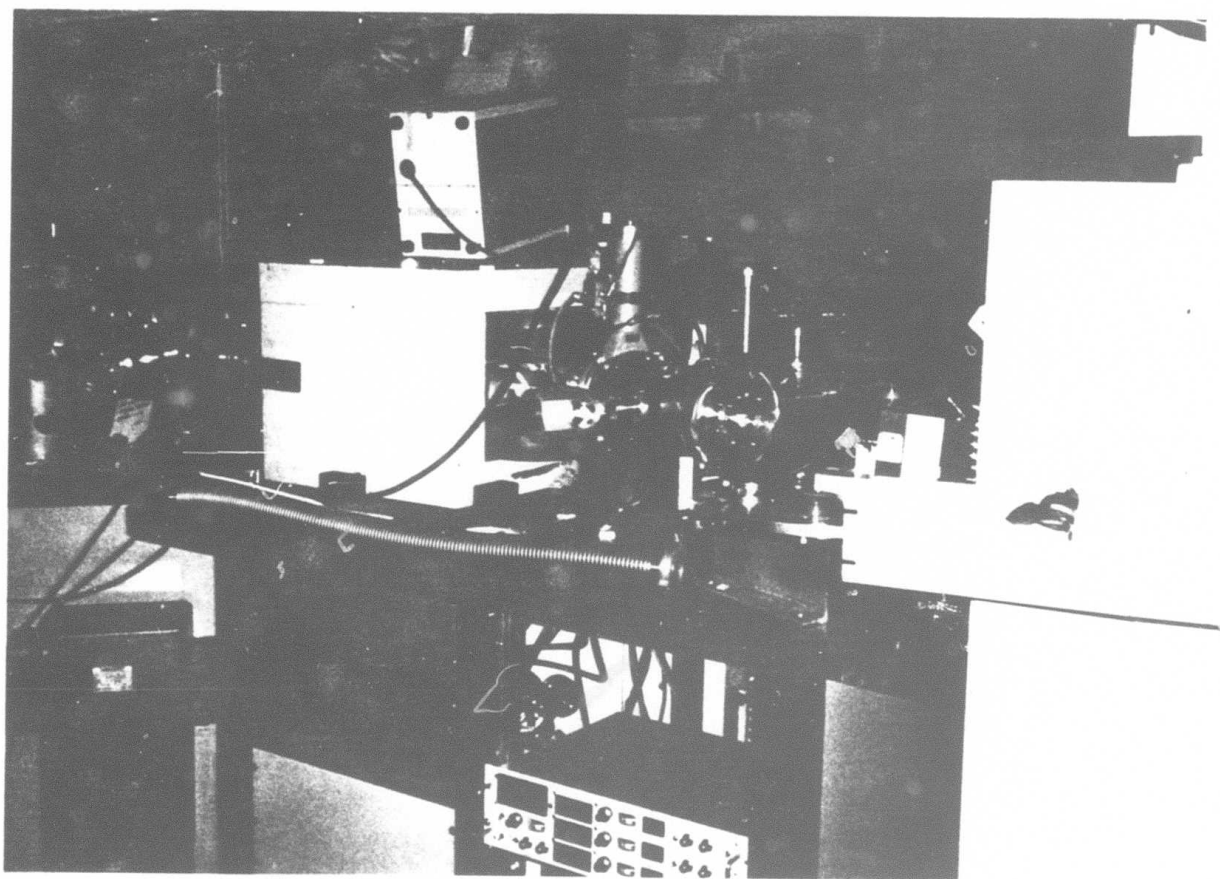


Fig.5 (b)

state 3 MeV, etc. The net energy, E , of the ions exiting the accelerator for atomic ion injection neglecting any ion source bias is thus given by

$$1) \quad E = (1 + q)eV$$

where q is the charge state of the "stripped" positive ion, e is the unit electronic charge and V is the terminal voltage.

A complication arises when molecular ions are injected into the accelerator either intentionally or unintentionally. Again multiply charged species will be formed, but in this case, initially multiply charged molecular complexes corresponding to the removal of 3, 4, 5, . . . , n electrons. Except in extraordinary circumstances (resonant stability) most multiply charged molecules will be unstable and will spontaneously dissociate in the stripper canal due to Coulomb repulsion. Other molecules will dissociate by simple collisional dissociation processes. When a dissociation event occurs, the fragment energy, E_i , of the i -th fragment ion after full acceleration by the tandem will be given by:

$$2) \quad E_i = (m_i/M + q_i)eV$$

where q_i is the charge of the i -th fragment ion after stripping, M is the mass of the injected negative molecular ion, m_i is the mass of the i -th positive ion fragment and V is the terminal voltage. Thus the exiting beam for a given injected negative molecular ion will consist primarily of atomic species with various energies, charge states and masses. The objective of the analysis is to unambiguously identify a particular species through a process referred to as mass and charge spectroscopy. In this regard it is helpful to choose a prime positive charge state relative to the mass of interest (e.g., +3). The use of the higher charge states ($> +2$) is advantageous in eliminating molecular ion interferences because many examples of stable, doubly positive charged molecules have been found (22).

If we intentionally inject a negative molecular ion (e.g., SiAs^-) there will be a uniquely defined solution to the equations of motion for the +3 species of interest (As^{+3} in this case) through the various ion optical elements of the instrument. When analyzing materials in a survey mode care must be exercised in choosing the injected ion as well as the charge state of the stripped atomic ion for optimization of specificity and sensitivity. The relationship between final ion energy and final charge state for purely atomic injected species is given by Equation 2 when $m_i = M$, thus reducing to Equation 1 as required.

A second complication in the high energy spectroscopy that impacts hardware requirements and operating procedures involves instrument tuning and how one goes about isolating a particular species (energy, mass and charge state). In an electrostatic deflection system the transverse force (electrostatic potential) required to deflect a moving charged particle a given distance varies directly with the particle energy and inversely with the charge state. Therefore, the quadrupole lens field (focussing) and ESA voltage (deflection) will track as the energy (terminal voltage) or charge state of the particle is changed while preserving beam focus and deflection through the ESA exit slit. This feature can be used to quickly "tune" the system for different isotopes or elements within a modest mass range. It is preferable to use the electrostatics of the system for mass selection because of difficulties associated with tuning the strong focusing magnets. Therefore, the system is designed so that four independent terminal and ESA/quadrupole voltages can be preset and then selected during an analysis using a switch panel at the operating console. This procedure, colloquially known as "bouncing," allows a single magnetic field to be used for particles with different masses. Mass and charge identification is accomplished by changing the terminal voltage (energy of the particles) so that the radius of curvature in a fixed magnetic field is the same for each species.

III. Experimental Samples

All of the experiments designed for this initial evaluation focused on Si as the matrix material. Wafer samples were provided by Dr. Richard Hockett of Monsanto, a collaborator in this study, with known doping levels of boron, phosphorus, arsenic, antimony and iron. High purity, undoped float-zone silicon was used as a "blank." Dopant concentrations ranged from about 10^{20} atm-cm^{-3} to $< 10^{14}$ atm-cm^{-3} whenever possible so that working curves of detected signal versus concentration could be generated over the largest possible concentration range. Boron was included because it is one of the most sensitive dopants by conventional SIMS (oxygen bombardment/positive secondary ion spectrometry) and is interference-free, while having only a moderate electron affinity. The n-dopants, on the other hand, all have favorable electron affinities and suffer varying degrees of molecular ion interferences in conventional SIMS (cesium ion bombardment/negative secondary ion spectrometry). Iron is a hybrid situation in the sense that it is a poor negative ion former and suffers a major interference in conventional positive ion spectroscopy SIMS from a matrix dimer ion ($^{28}\text{Si}_2^+$). It was hoped that a sufficiently large molecular ion signal such as FeO^- or FeSi^- might be generated under cesium ion bombardment so as to circumvent the unfavorable electron affinity of atomic iron. This is one way of generating negative ions

for elements with inherently unfavorable electron affinities. (We will discuss another method later in the report.) This same basic approach is commonly employed in conventional SIMS for the analysis of nitrogen in silicon using SiN^- as the analyte species with Cs^+ bombardment.

All of the impurity elements chosen for this study have intrinsic technological importance at concentrations well below the detection limits currently attainable by conventional SIMS. Table 2 provides a summary of the samples used with carrier concentrations and other sample parameters provided by Dr. Hockett.

Table 2

Samples Analyzed

Sample #	Orientation	Type	Resistivity ($\Omega\text{-cm}$)	Dopant	Carrier Concentration
1	$\langle 111 \rangle$	n	300-900	none*	$< 1 \times 10^{13}$
2	$\langle 111 \rangle$	p	0.008-0.025	B	$4 \times 10^{18} - 1 \times 10^{19}$
3	$\langle 111 \rangle$	n	0.005-0.020	Sb	$1 - 9 \times 10^{18}$
4	$\langle 100 \rangle$?	14-16	As	1×10^{14}
5	$\langle 100 \rangle$	n	20	Sb	1×10^{14}
6	?	?	?	Fe	1×10^{20}
7	$\langle 111 \rangle$	p	1.5-2.5	B	$5 \times 10^{15} - 1 \times 10^{16}$
					(see text)
8	$\langle 100 \rangle$	n	0.009-0.022	P	$1 - 4 \times 10^{18}$
9	$\langle 111 \rangle$	p	0.06-0.25	B	$5 \times 10^{17} - 1 \times 10^{18}$
10	$\langle 100 \rangle$	n	0.9-1.8	P	$2 - 3 \times 10^{16}$
11	$\langle 111 \rangle$	n	0.2-0.3	P	$2 - 3 \times 10^{16}$
12	?	?	?	As	7×10^{19}

* Float zone Si "background" check.

? Data not available

IV. Experimental Results

Figure 6 graphically illustrates the fundamental advantage of AB/SIMS compared to conventional SIMS. Figure 6A shows a survey negative ion mass spectrum

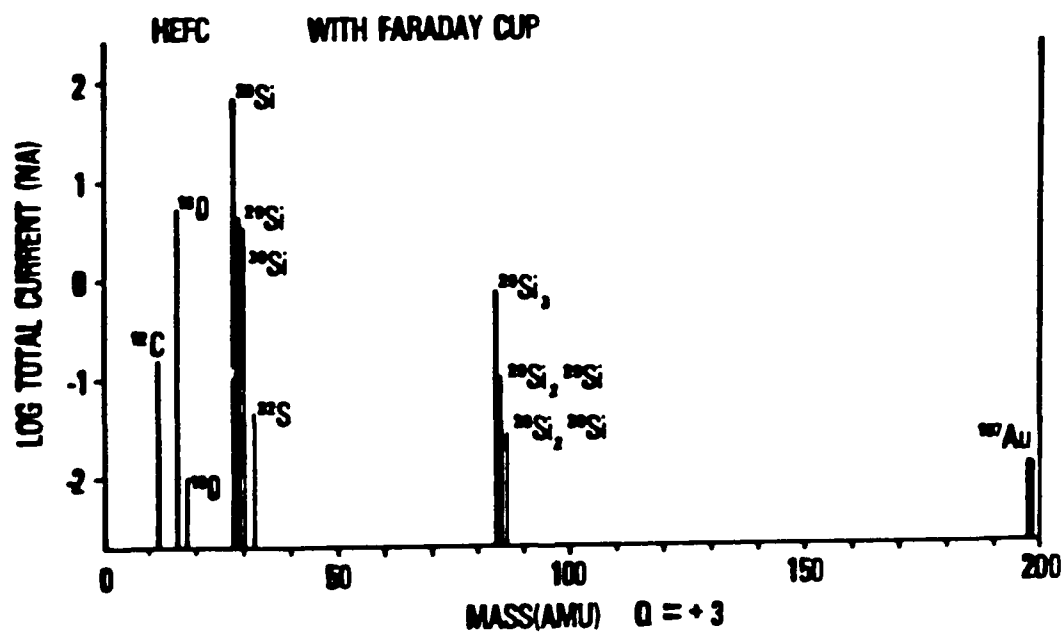
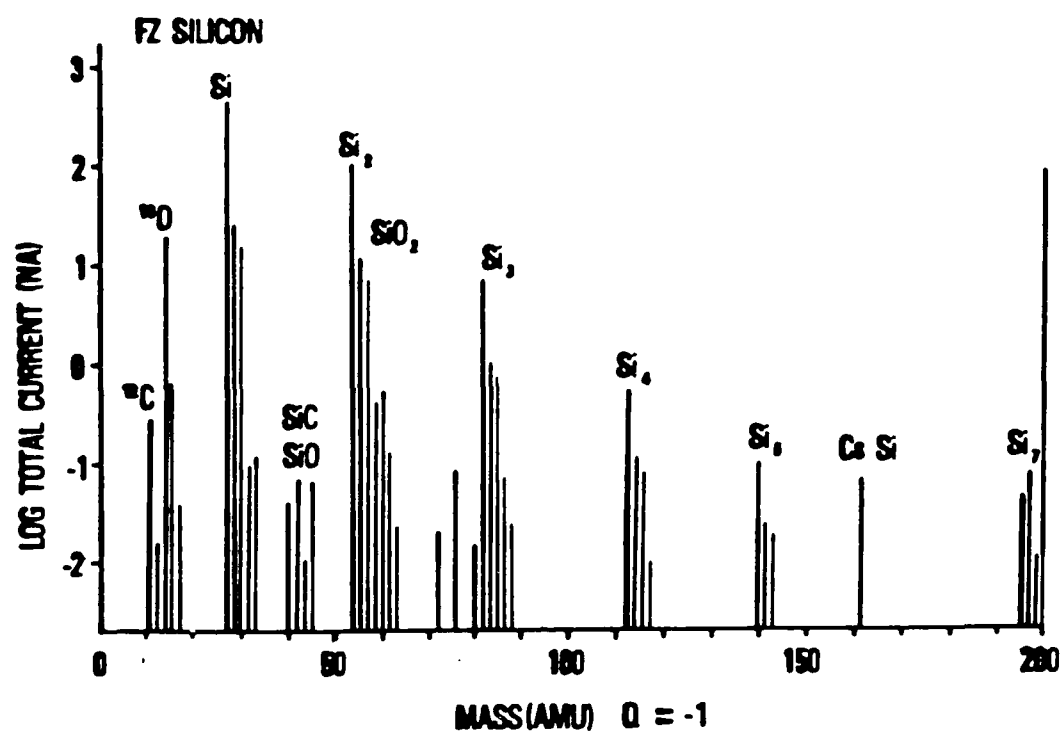


Fig.6

taken from float zone silicon using the low energy Faraday cup positioned just before the tandem accelerator. This simulates a conventional negative ion spectroscopy SIMS analysis. A host of molecular ions can be seen, including polymeric silicon ($^{28}\text{Si}_7^-$, for example, is readily detected), oxides and carbides of silicon ($^{28}\text{Si}^{12}\text{C}^-$ and $^{28}\text{Si}^{16}\text{O}^-$ are typical), a complex of the matrix and primary beam species ($^{133}\text{Cs}^{28}\text{Si}^-$), hydrides such as $^{28}\text{Si}_3^{30}\text{Si}^1\text{H}^-$ at mass 115 amu and a number of other peaks not readily identifiable. We can be reasonably certain that no impurity peaks are present in this spectrum due to the ultra high purity of undoped float zone silicon. In contrast, Figure 6B shows a mass spectrum acquired at the high energy Faraday cup behind the electrostatic analyzer after molecular dissociation induced by the stripping process. These data were obtained by injecting each low energy mass into the accelerator one by one and measuring the ion current at the high energy end observed for the +3 charge state exiting the accelerator as a function of injected mass. In addition to the silicon isotopes, we detect carbon, the isotopes of oxygen, the major sulphur isotope (32 amu) and gold. Carbon and oxygen most likely arise from residual vacuum contamination. The sulphur and gold impurities, on the other hand, would appear to be real. However, the sample analyzed just prior to our experiments was a meteoritic iron sulfide nodule which had been gold coated to alleviate specimen charging. (Both gold and sulfur readily form negative ions.) Thus, the impurity species detected in the FZ- silicon spectrum are undoubtedly occurring as a "memory" effect despite the fact that the source was cleaned before loading the sample used in this experiment. Memory effects are generic to all types of mass spectrometry ion sources, so we are not surprised by the observation. However, it is noteworthy that we are able to readily detect these minor impurity signals, attesting to the sensitivity of the AB/SIMS technique.

We can calculate isotopic abundances for oxygen and silicon from the atomic ion peak heights in Figure 6B as shown in Table 3:

Table 3

<u>Isotope</u>	<u>Measured Abundance (%)</u>	<u>Theoretical Abundance (%)</u>
^{16}O	99.82	99.76
^{18}O	0.19	0.20
^{28}Si	89.8	92.2
^{29}Si	5.5	4.7
^{30}Si	4.6	3.1

Given that these are single measurements taken in an analog survey scanning mode, the relative abundances are quite satisfactory. Better accuracy could easily be achieved if isotope ratio was actually the parameter of interest.

The only other measurable peaks in the high energy spectrum shown in Figure 6B are attributable to triply charged trimer molecular ions of silicon. There seems to be an ion stability "resonance" that occurs when the number of atoms in the polymeric molecule equals the charge state. This stability resonance probably comes about from an equipartitioning of charge producing a highly symmetrized mass/charge structure. Note the complete absence of dimer, tetramer, etc., clusters and Si_xO_y combinations which routinely plague conventional SIMS analysis.

An important consideration in assessing the "ultimate" detection sensitivity of AB/SIMS is the transmission of the low energy mass filtering system and the effective transmission of the injected negative ion beam through the accelerator. A typical $^{28}\text{Si}^-$ ion current measured at the low energy Faraday cup on the Toronto AB/SIMS machine ranged from about 0.2 - 1 microamp. By comparison, the Cameca IMS-3f operated in the low mass resolution mode ($M/\Delta M = 500$) will deliver a $^{28}\text{Si}^-$ ion current of nominally the same amount including an additional energy filtering of the secondary ion beam by an ESA! Although no detailed measurements of sample consumption were made, it appeared that more material was consumed per unit time to achieve the 1 microamp of $^{28}\text{Si}^-$ beam on the Toronto instrument than we routinely require in a bulk silicon analysis using the Cameca IMS-3f. The implication is that the efficiency of ion extraction and transmission of the low energy end of the isotrace AB/SIMS system is inferior to that achieved by Cameca in the IMS-3f ion microanalyzer. Admittedly there is a considerable price differential between the two mass spectrometers, but a compromise in detection limits arises from current losses through the magnetic analyzer.

Once the mass separated negative ion beam is injected into the accelerator, losses due to angular divergence are virtually eliminated by phase space compression as discussed previously. Scattering events will occur in the stripper canal giving rise to an average increase in transverse momentum in the beam, but based on impact parameter considerations, the probability of large angular deviations will be small. Phase space compression occurs again through the second acceleration leg of the tandem, this time involving multiplication of the terminal voltage by the charge state of the positive ion. Hence, divergence losses through the entire accelerator are nearly zero.

Some "losses" will occur through the accelerator because of the formation of a distribution of charge states and energies for each ion arising from the

charge stripping process . If we were able to inject pure $^{28}\text{Si}^-$ at the low energy end, as mentioned earlier, we would observe ion currents for Si^+ , Si^{+2} , Si^{+3} , ..., Si^{+n} where n could be as large as 10 to 14 depending upon the exact stripping conditions. Carbon, of course, could not exceed a charge state of +6 (fully stripped). Each charge state will have its own characteristic energy when it exits the accelerator (Equation 1). If the injected ion is a single atomic species or is dominated by a single atomic component one would not need to discriminate among the various charge states and energies produced, but rather could make an integral measurement that would be quite useful. However, for analysis of an impurity species at the same mass as an intense molecular ion interference, one must be able to perform charge, energy and mass spectrometry on the high energy ions to resolve the analyte species of interest from the molecular dissociation fragmentation products.

The above point is important in AB/SIMS analysis and is best illustrated by a simple example. Let us consider the situation of analyzing trace-level iron in silicon. For the sake of argument let us assume equal negative ion yields for the two species, although we know a priori that iron is a very poor negative ion former relative to silicon. Let us further assume that the iron concentration in the silicon matrix is such that the ion currents for $^{28}\text{Si}_2^-$ and $^{56}\text{Fe}^-$ are 100 to 1, i.e., there are 100 times more silicon molecular ions than iron atomic ions. These ions, both at nominal mass 56 amu, are difficult to resolve in a conventional high performance SIMS mass spectrum and are unresolvable in the low energy end of the Isotrace AB/SIMS system. When the injected beam of $^{28}\text{Si}_2^-$ and $^{56}\text{Fe}^-$ enter the gas stripper canal, essentially all of the molecules will be dissociated to atomic silicon ions in various charge states. The iron components of the beam will exhibit a charge state distribution as well. Consequently, the beam exiting the accelerator will consist of Si^+ , Si^{+2} , ..., Si^{+n} , Fe^+ , Fe^{+2} , ..., Fe^{+n} , all at different energies. Our interests are in only the iron ions. To achieve the required separation, we can perform energy spectroscopy because the Si^{+n} ion energies will necessarily differ from the corresponding iron ion energies at the same charge state due to energy partitioning at the time of dissociation. This is to say that at the instant of dissociation, each silicon atom will carry away half of the molecular kinetic energy at that point while the iron ions will retain all of the kinetic energy gained through the front leg of the tandem. For a 2 MV terminal voltage, Si^+ would exit with 3 MeV energy (1 MeV at dissociation plus 2 MeV after additional acceleration), Si^{+2} would have 5 MeV, etc., while Fe^+ would have 4 MeV, Fe^{+2} would have 6 MeV, and so forth. Were we to energy analyze the exiting beam with a solid state particle detector we would observe a series of peaks in a multichannel analyzer energy spectrum corresponding to each discrete energy. Alternatively, in this same example we could isolate a single species by means of an electrostatic analyzer and a slit provided the

ESA had sufficient energy resolution (not a serious constraint in this case). For general purpose work the ESA approach is preferable due to resolution considerations and the fact that particle detectors lack durability when subjected to intense bombardment by energetic heavy ions. (Detector consumption was something of a problem during the course of these experiments.)

In the above example it is a straightforward matter to separate the desired analytical signal from the unwanted interference. In a more general sense, however, matters are not so simple. A common problem in conventional SIMS is the analysis of phosphorus in silicon. Here the difficulty arises from a hydride molecular ion, $^{30}\text{Si}^1\text{H}^-$ at the same nominal mass as $^{31}\text{P}^-$. The species produced by the stripper canal in AB/SIMS will be H^+ , $^{30}\text{Si}^+$, $^{30}\text{Si}^{2+}$, ..., $^{31}\text{P}^+$, $^{31}\text{P}^{+2}$, ... and possibly other Si isotopes arising from $^{29}\text{Si}^1\text{H}_2^-$ and $^{28}\text{Si}^1\text{H}_3^-$. Figure 7 shows a high mass resolution spectrum from mass 28 amu through mass 31 amu taken with a Cameca IMS-3f from a phosphorus doped amorphous silicon hydride solar cell sample. Mass 28 amu exhibits a singlet peak corresponding to $^{28}\text{Si}^-$. Mass 29 amu exhibits two peaks corresponding to $^{29}\text{Si}^-$ and $^{28}\text{Si}^1\text{H}^-$ while mass 30 amu exhibits three peaks including $^{30}\text{Si}^-$, $^{29}\text{Si}^1\text{H}^-$ and $^{28}\text{Si}^1\text{H}_2^-$. Four peaks appear at mass 31 amu corresponding to $^{31}\text{P}^-$, $^{30}\text{Si}^1\text{H}^-$, $^{29}\text{Si}^1\text{H}_2^-$ and $^{28}\text{Si}^1\text{H}_3^-$. All four peaks would be injected together in the AB/SIMS instrument if the low energy mass spectrometer were tuned to mass 31 amu for this particular sample. Clearly the hydride molecular ions are very intense when large amounts of hydrogen are present. The magnitude of these interferences will scale with the intrinsic hydrogen content of the specimen and/or the partial pressures of hydrogen or hydrogenated gasses in the sample chamber residual vacuum.

Dissociation of the monohydride ($^{30}\text{Si}^1\text{H}^-$) in the stripper will give rise to an energy partitioning of 3.2% to the hydrogen and 97.8% to the silicon. These fractions will be the same for all charge states in accordance with Equation 2. Thus, for the +3 charge state and a 2 MV terminal voltage, $^{31}\text{P}^{+3}$ will occur at 8 MeV, and $^{30}\text{Si}^{+3}$ will occur at approximately 7.94 MeV. Given an intrinsic detector energy resolution of 15 keV and a statistical peak width in energy on the order of 30 keV (energy straggling) the two peaks will be barely resolvable, if at all, by a solid state detector. Similarly, in order to resolve these species in the post acceleration ESA, energy resolution must be quite good. The same sort of resolution constraint would apply if post acceleration magnetic analysis were employed in addition to the ESA due to the convolution of mass and energy in the high energy magnetic spectrometer. The analysis of phosphorus in silicon is further complicated by a common low

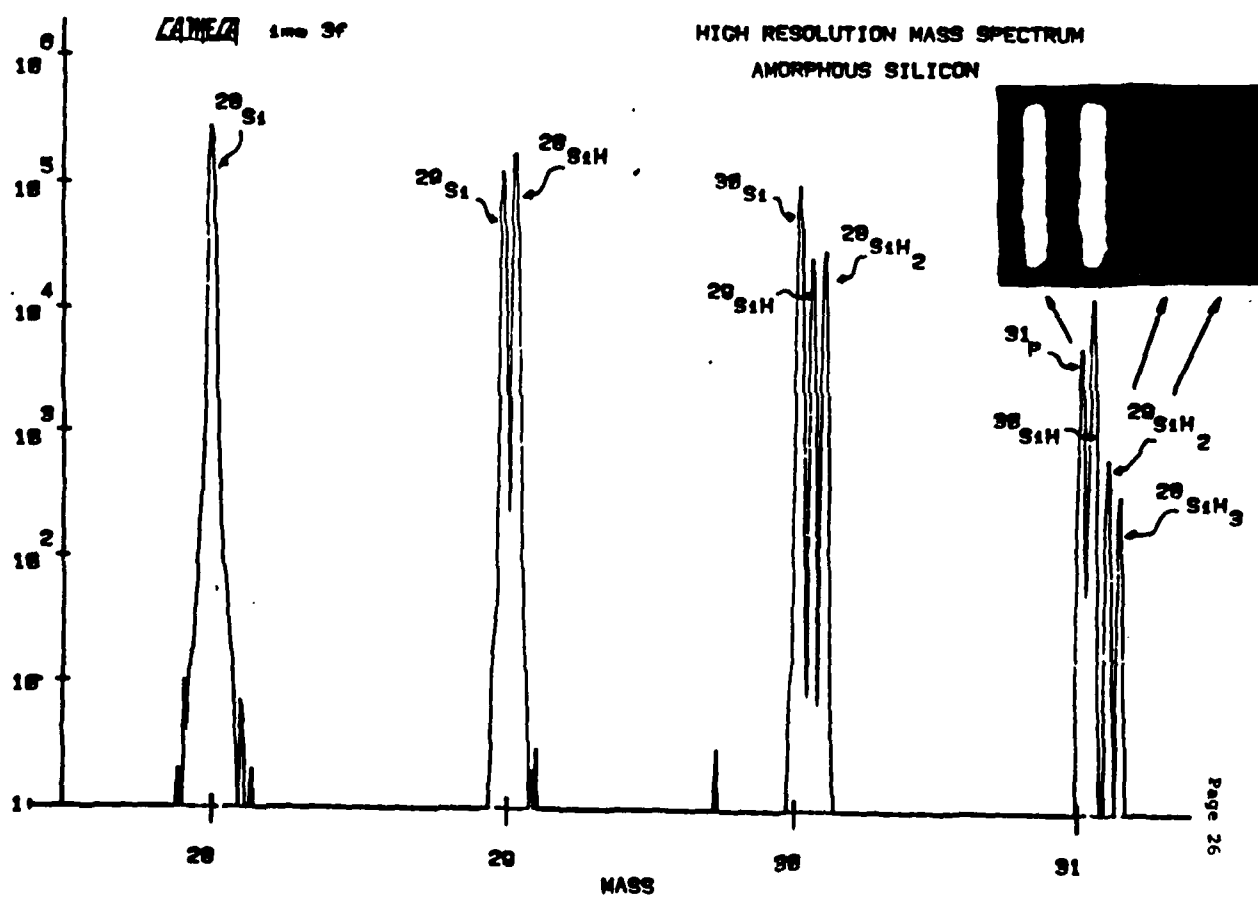


Fig.7

resolution mass spectrometry problem, i.e., abundance sensitivity. This problem comes about when a small peak to be measured is adjacent to a very large peak, e.g., $^{31}\text{P}^-$ beside $^{30}\text{Si}^-$. The Gaussian tail of the more intense peak can extend sufficiently in mass to overlap the mass region of the smaller peak. The low resolution magnetic mass spectrometer on the Toronto instrument appeared to have an abundance sensitivity on the order of 10^{-4} (i.e., the signal from the tail of the peak at the nominal mass of the species to be measured is no less than four orders of magnitude lower than the intensity of the peak top). The abundance sensitivity of the Cameca IMS-3f at high transmission is approximately 10^{-6} , at least two orders of magnitude superior to the Toronto instrument. Insufficient abundance sensitivity and/or an interference from monohydride dissociation precluded our making any meaningful measurements of phosphorus in silicon using the Isotrace machine.

A. Boron in Silicon

Our experiments were begun with boron in silicon because of its freedom from molecular ion interferences and its moderately favorable electron affinity. The highest doping concentration ($1 \times 10^{19} \text{ atm-cm}^{-3}$) was the first sample analyzed so as to provide a boron secondary ion beam of sufficient intensity to tune the instrument. The $^{11}\text{B}/^{10}\text{B}$ isotope ratio served as an aid in qualitative identification of the respective signals. Initially, data were taken behind the high energy ESA without using either high energy bending magnets. For the purpose of quantitation, $^{28}\text{Si}^{+3}$ was measured at the high energy Faraday cup and a detector conversion factor obtained based on $^{16}\text{O}^{+3}$ measured on the Faraday cup and $^{18}\text{O}^{+3}$ measured on the particle detector assuming natural isotopic abundance. The sensitivity ratio of the two detectors generally ranged from 10 to 30 depending upon charge state. Data were collected for ^{10}B , ^{11}B and ^{28}Si using charge states +2, +3 and +4. The +5 charge state of boron (fully stripped) was found to be too low in intensity to be of any practical value. Signal integration times of 10 or 100 seconds were employed depending upon count rate so as to achieve reasonable counting statistics. The matrix ion intensity was recorded before and after each series of measurements to adjust for variations in overall system performance.

The actual experimentally acquired data, normalized impurity/matrix ratios, and measured boron isotopic abundances are shown in Table 4 for the four samples and three charge states investigated. Although two of the samples were alleged to have boron concentrations of nominally 7×10^{17} and $7 \times 10^{15} \text{ atm-cm}^{-3}$ respectively, all three sets of charge state data show the two samples to be comparable and roughly two orders of magnitude below that found for the highest concentration sample. Analysis of these same samples by

conventional SIMS using one of our Cameca IMS-3f ion microanalyzers (O_2^+ bombardment) gave $1.0 \times 10^{19} \text{ atm-cm}^{-3}$ for the highest concentration sample, $<3 \times 10^{14} \text{ atm-cm}^{-3}$ for the float zone specimen and $2 \times 10^{17} \text{ atm-cm}^{-3}$ for both of the other two samples. This was discouraging in the sense that some form of sample mix-up must have occurred, leaving only two unique boron concentrations along with the float zone silicon blank. However, it was encouraging to see that, in fact, we were performing an "analysis" and obtaining meaningful results using the AB/SIMS technique on our first attempt!

Table 4

<u>Sample</u>	<u>Charge State</u>	<u>$^{10}\text{B}^{+3}$ (cps)</u>	<u>$^{11}\text{B}^{+3}$ (cps)</u>	<u>$^{28}\text{Si}^-$ (namp)</u>
Float Zone	+2	29	612	150
7×10^{18}	+2	818	2438	3
7×10^{17}	+2	976	3670	180
7×10^{15}	+2	1385	5075	200
Float Zone	+3	51	2012	640
7×10^{18}	+3	2443	7234	4
7×10^{17}	+3	3064	8750	450
7×10^{15}	+3	5667	9429	500
Float Zone	+4	n.d.	1.2	50
7×10^{18}	+4	7000	16,700	80
7×10^{17}	+4	64	170	32
7×10^{15}	+4	97	193	54

<u>Sample</u>	<u>Charge State</u>	<u>$^{10}\text{B}/^{28}\text{Si}$</u>	<u>$^{11}\text{B}/^{28}\text{Si}$</u>	<u>$^{11}\text{B}/^{10}\text{B}$</u>
Float Zone	+2	4.4×10^{-9}	9.4×10^{-8}	21.4
7×10^{18}	+2	6.3×10^{-6}	1.9×10^{-5}	3.0
7×10^{17}	+2	1.2×10^{-7}	4.7×10^{-7}	3.9
7×10^{15}	+2	1.6×10^{-7}	5.8×10^{-7}	3.6
Float Zone	+3	5.8×10^{-10}	1.9×10^{-8}	32.8
7×10^{18}	+3	3.7×10^{-6}	1.1×10^{-5}	3.0
7×10^{17}	+3	4.2×10^{-8}	1.2×10^{-7}	2.9
7×10^{15}	+3	6.9×10^{-8}	1.2×10^{-7}	1.7
Float Zone	+4	n.d.	5.5×10^{-10}	-
7×10^{18}	+4	2.0×10^{-6}	4.8×10^{-6}	2.4
7×10^{17}	+4	4.6×10^{-8}	1.2×10^{-7}	2.6
7×10^{15}	+4	4.0×10^{-8}	8.2×10^{-8}	2.1

n.d. = not detected

The boron isotope ratio data were somewhat curious at the time they were computed. All of the heavily doped samples gave isotopic ratios in reasonable agreement with the literature value ($^{11}\text{B}/^{10}\text{B} = 4$). A slight systematic deviation was noted which we attributed to mass fractionation, a common problem in any isotope ratio measurement. However, the float zone sample which presumably contained no boron ($< 3 \times 10^{14} \text{ atm-cm}^{-3}$) still showed measurable signals for both ^{10}B and ^{11}B , but with an isotope ratio differing from natural abundance by a factor of five (high ^{11}B). No satisfactory explanation was immediately forthcoming. The initial presumption was made that possibly some spurious species such as ^{12}C or a random scattered beam was inadvertently reaching the detector and grossly skewing the results. Additional measurements were made using first one and then both of the high energy magnetic analyzers in an effort to resolve the dilemma. The signals remained essentially constant although some decrease in the $^{11}\text{B}/^{10}\text{B}$ ratio was noted with sputtering time. It was later discovered that an enriched ^{11}B sample had been extensively analyzed shortly before our arrival in Toronto. Once again we were detecting a "memory" signal from a prior matrix which persisted after source cleaning and was measurable due to the ultra-sensitive detection capabilities of the AB/SIMS system. At higher concentrations the isotope ratios were virtually unaffected because the boron signals from the samples were 100 times the signals from the memory effect. Hence the "background" interference was overwhelmed in every case but the float zone silicon. The detailed quantitative detection limit results for boron will be discussed along with the arsenic and antimony data in a later summary section.

B. Arsenic in Silicon

Conventional SIMS measurements of arsenic in silicon tend to be limited at the lower concentrations by molecular ion interferences, primarily $^{29}\text{Si}^{30}\text{Si}^{16}\text{O}^-$ and/or $^{28}\text{Si}^{30}\text{Si}^{16}\text{O}^{1-}$. Since arsenic is monoisotopic, one is forced to contend with these interferences which arise naturally from the silicon matrix and residual vacuum contaminants or oxygen intrinsic to the specimen (Cz-Si). Either high mass resolution or energy discrimination techniques can be employed with the IMS-3f to minimize the effect of these interferences, but both lead to a significant reduction in the $^{75}\text{As}^-$ signal intensity and a corresponding degradation in detection limits compared to the "interference-free" case.

Measurements of arsenic in silicon by AB/SIMS were made for three different samples. Two were bulk doped to levels of $7 \times 10^{19} \text{ atm-cm}^{-3}$ and $1 \times 10^{14} \text{ atm-cm}^{-3}$, respectively, and the third was the float-zone silicon "blank." Three different detection configurations were used in the course of the arsenic

experiments. For this reason, the data obtained from the arsenic analysis can be used to evaluate each of these detection methods to determine which might give the best ultimate detection limit for the Isotracer machine. In addition, these data can be used to aid in the comparison of data taken for other impurity elements where only one of the various detection methods was used. The three detection methods are:

1. Atomic ion injection of $^{75}\text{As}^-$ at mass 75 amu with high energy electrostatic filtering,
2. Atomic injection of $^{75}\text{As}^-$ with high energy electrostatic filtering, post acceleration foil stripping to increase the ion charge state followed by magnetic filtering, and
3. Molecular injection ($^{75}\text{As}^{28}\text{Si}^-$) with molecular dissociation at the terminal followed by high energy electrostatic filtering, foil stripping and final magnetic analysis.

Foil stripping prior to final magnetic filtering is required at the high energy end for the heavier elements on the Isotracer machine because the strong focusing magnets are limited in terms of mass-energy product per unit charge. Because of this limitation, the highest tolerable energy for a +3 arsenic ion which could be transmitted through the magnets is 2.88 MeV. To obtain this particle energy the terminal voltage would have to be lowered to 2.88/4 or 720 keV. At this energy the production of +3 ions in the stripper is severely reduced, thereby degrading detection limits. If the terminal voltage is raised to 2 MV the energy of the resulting +3 ion will be 8 MeV exceeding the magnet limit. By further charge stripping the $^{75}\text{As}^{+3}$ ion to a higher charge state after full acceleration, the particle could be analyzed using the magnets because of the resulting lower magnetic rigidity. The lowest charge state for arsenic which meets the mass/energy criterion is +5.

There are several drawbacks to producing high charge state ions by foil stripping including beam energy straggling, increased spatial divergence of the beam and loss of signal due to populating a large number of different charge states each with moderate probability. The typical fraction of ions produced in any one charge state is usually less than 25% of the total incident beam. However, the count rate loss due to foil stripping is less than the loss caused by lowering the terminal voltage to 720 KV. For this reason it was decided that when high energy magnetic filtering was to be used prior to detection, the foil stripper method would be employed.

Tables 5 and 6 show the charge state distributions observed for the As^{+3} ion after foil stripping with As^- and AsSi^- injection. The most highly populated

states are, respectively, +9 and +6. Injection of As^- followed by foil stripping to a charge state of +10 gave the optimum arsenic detection limit based on these preliminary measurements. Again the detailed quantitative results will be reserved for a later comparative summary section.

Table 5

Charge State Distribution
After Foil Stripping, As^- Injection

<u>Charge State</u>	<u>%</u>
+16	0.016
+15	0.244
+14	1.242
+13	5.428
+12	13.377
+11	13.377
+10	22.540
+ 9	22.641
+ 8	14.087
+ 7	5.740
+ 6	1.279
+ 5	<u>0.028</u>
	99.999

Table 6

Charge State Distribution After Foil Stripping,
AsSi⁻ Injection

<u>Charge State</u>	<u>%</u>
+13	0.010
+12	0.081
+11	0.642
+10	2.489
+ 9	9.062
+ 8	15.074
+ 7	25.367
+ 6	25.884
+ 5	16.629
+ 4	<u>4.761</u>
	99.999

C. Antimony in Silicon

The antimony study proceeded along the same lines as the arsenic analysis. High and low concentration bulk-doped silicon material ($5 \times 10^{18} \text{ atm-cm}^{-3}$ and $1 \times 10^{14} \text{ atm-cm}^{-3}$, respectively) and the float-zone silicon blank constituted the sample set to be investigated. Like arsenic, it was found that large, unintelligible beams were detected after the ESA using the straight through port. However, as was also the case with arsenic, a charge state higher than +3 was required to bend the beam through the high energy filtering magnets. A stripper foil was employed after full acceleration to achieve the necessary elevated charge state. Although it was not optimal, the analytical combination used was Sb⁺³ from the accelerator and Sb⁺⁶ after foil stripping. The +6 component of the distribution was later found to represent about 5% of the incident Sb⁺³ beam, which we can treat as an effective foil "transmission." Table 7 shows the experimental results obtained. Multiple measurements were made with the variation from measurement to measurement being on the order of counting statistics ($N^{1/2}$). The antimony isotopic abundance values for the highest concentration sample are 56% ¹²¹Sb and 44% ¹²³Sb, in reasonable agreement with the literature values of 57.2 and 42.8%, respectively.

Table 7

Sample Sb	$^{121}\text{Sb}^{+6}$	$^{123}\text{Sb}^{+6}$	$^{28}\text{Si}^{-}$	$^{121}\text{Sb}^{+6}/^{28}\text{Si}^{-}$
Concentration(atm-cm-3)	(cps)	(cps)	(namp)	
5×10^{18}	10,442	8189	440	23.7
1×10^{14}	2.2	not measured	615	0.0036
Float Zone	0.6	not measured	790	0.00076

D. Phosphorus in Silicon

As was briefly mentioned previously, no useful data could be obtained for phosphorus in silicon. Several attempts were made using a variety of different approaches. None of these were successful, probably because of the abundance sensitivity problem and/or insufficient energy resolution at the high energy ESA to resolve $^{31}\text{P}^{+3}$ from the hydride molecular dissociation fragment ion, $^{30}\text{Si}^{+3}$. The Isotrace Laboratory personnel all complained about these limitations, but conceded that for ^{14}C work (their dominant mission) the present instrumental configuration is adequate. We were somewhat surprised to learn that researchers at Texas Instruments (23), using the machine at the University of Arizona, have published results for phosphorus in silicon using an approach similar to that employed in these studies, i.e., analyzing a series of samples of known concentration ranging from about 10^{19} to 10^{14} atm-cm $^{-3}$. The Arizona instrument is very similar to the one at the University of Toronto, particularly in regards to the low energy mass spectrometer. In recent conversations with University of Arizona AB/SIMS staff, it has been learned that efforts to repeat the TI measurements have, to date, been unsuccessful. Suffice it to say that given present instrumentation, the analysis of phosphorus in silicon by AB/SIMS is at best extremely difficult and apparently irreproducible. The problem could be solved, however, by a redesign of the low energy mass spectrometer with high transmission, high abundance sensitivity and broad elemental coverage in mind such as has been done with the Cameca IMS-3f.

E. Iron in Silicon

Iron was included in these initial experiments realizing full well that because of the unfavorable electron affinity situation, inadequate Fe^{-} signal might be produced by the Cs^{+} sputtering beam to perform an analysis. However, it was thought that due to the only moderately high vacuum in the source region (10^{-6} to 10^{-7} Torr), there might be sufficient FeO^{-} produced to allow molecular ion injection analogous to the use of AsSi^{-} . The sample employed in

this experiment was a bulk doped, dilute alloy with an iron concentration of approximately 2000 ppma ($1 \times 10^{20} \text{ atm-cm}^{-3}$). Conventional SIMS analysis had previously shown the iron to be inhomogeneously distributed on a micron scale owing to the high impurity concentration. On the scale of the AB/SIMS measurements, however, the material should appear homogeneous. In the previous analyses (boron, arsenic, antimony and phosphorus), a high concentration sample capable of producing intense dopant ion beams was initially analyzed to set the numerous instrumental parameters necessary to transport a particular species from the source to the final detector. In essence these samples provided a "pilot" beam absolutely critical for instrument tuning. This was not available for iron because the molecular ion signals were simply too low in intensity to easily detect and follow along the ion optical path. Furthermore, the intensity of FeO^- could have been substantially increased by leaking oxygen into the sample chamber region as has been done in the past in conventional SIMS instruments with Ar^+ ion bombardment, but such provisions were not available in the Toronto source configuration. Thus no data were obtained for iron in silicon other than to conclude that it will have to be done in a nonroutine way. Interestingly, the University of Toronto staff have been able to analyze ^{26}Al concentrations down to 1 part in 10^{14} ($5 \times 10^8 \text{ atm-cm}^{-3}$). To make Al^- , they first generated Al^+ , a readily formed ion, then used gas phase charge exchange in a lithium vapor canal to convert Al^+ to Al^- . A similar system is employed in our GIC Rutherford backscattering tandem accelerator to produce He^- . The process should be equally effective for elements like iron where sputtered Fe^+ can be converted to Fe^- by vapor phase charge exchange.

F. Quantitation Summary for Boron, Arsenic and Antimony in Silicon

Figure 8 shows a plot of normalized signal intensity versus concentration based on the data obtained for the boron, arsenic, antimony and high purity float-zone silicon samples listed in Table II. Beginning with boron, because of the anomalously high ^{11}B background, the results for ^{10}B give us the best estimate of extrapolated detection limit. From the measured "background," these values are $7 \times 10^{15} \text{ atm-cm}^{-3}$ for the +2 charge state, $2 \times 10^{15} \text{ atm-cm}^{-3}$ for the +3 charge state and $1 \times 10^{15} \text{ atm-cm}^{-3}$ (from ^{11}B data) for the +4 charge state. Provided the memory effect could be eliminated and taking 0.1 counts per second (10 counts in 100 seconds) as a "cosmic-radiation" background, the ultimate detection limit can be extrapolated from observed count rates to be about $5 \times 10^{12} \text{ atm-cm}^{-3}$ based on the $^{10}\text{B}^{+3}$ results. Conceivably, ^{11}B could give an even lower value on the order of $1 \times 10^{12} \text{ atm-cm}^{-3}$. As an atomic fraction, this would be equivalent to two parts in 10^{11} or 20 parts per trillion (ppt). We hasten to add that this extrapolation is

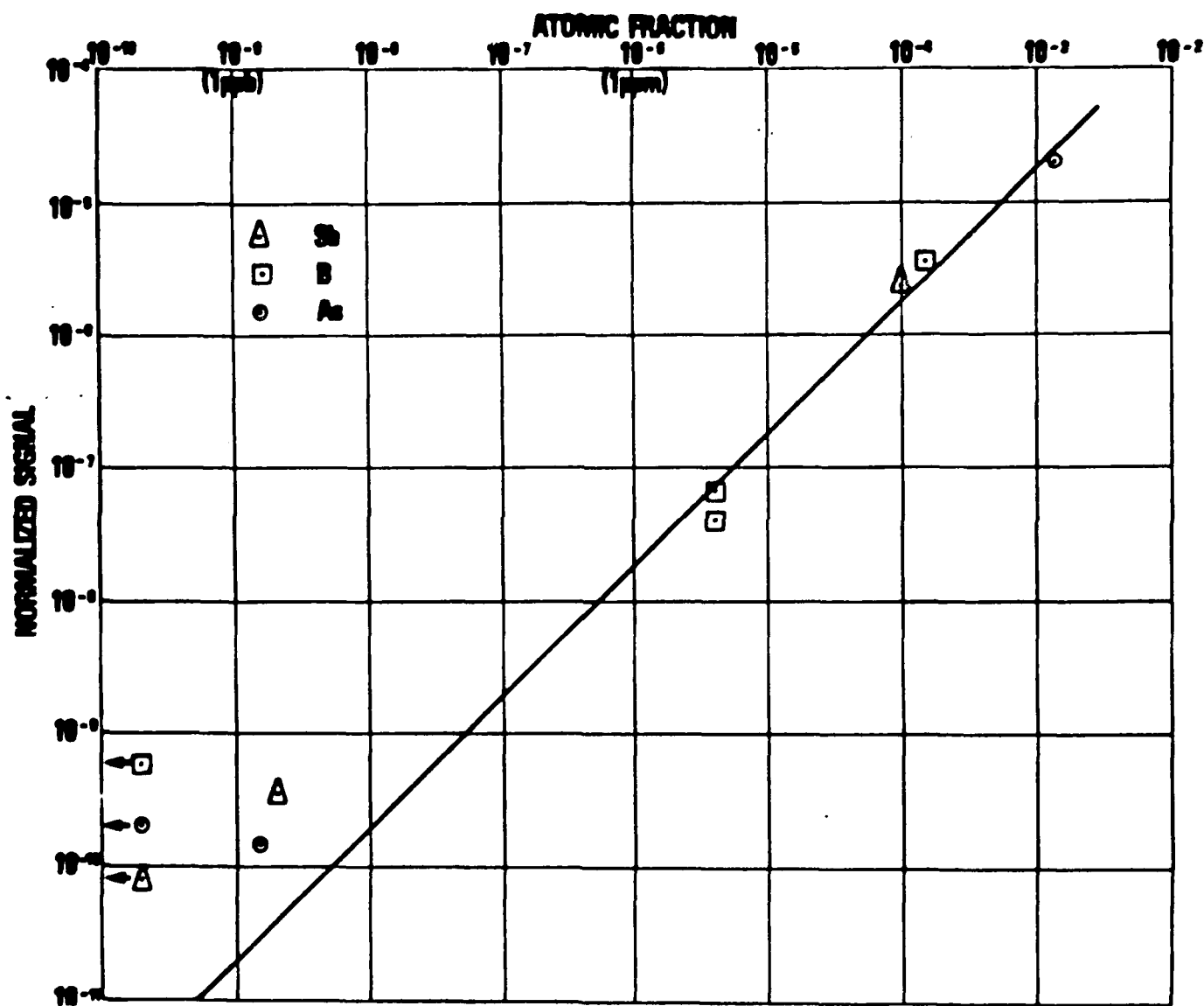


Fig.8

for an element with only a moderately favorable electron affinity and with little effort expended in terms of analysis optimization. As stated previously, boron is best analyzed by conventional SIMS using oxygen ion bombardment and positive secondary ion spectroscopy. Under those conditions our detection limit with the IMS-3f is approximately 1×10^{13} atm-cm⁻³. By cesium ion bombardment the Cameca detection limit is on the order of 1×10^{15} atm-cm⁻³ and is limited by available signal. More favorable negative ion formers, e.g., arsenic, should give better detection limits than 10^{12} atm-cm⁻³ using the AB/SIMS technique just based on electron affinity considerations, all other things being equal.

The observed count rate corresponding to an arsenic concentration of 4×10^{14} atm-cm⁻³ was roughly 320 cps using ⁷⁵As⁻ injection and As⁺³ from the accelerator, foil stripped to As⁺¹⁰. For our 0.1 cps cosmic radiation background this would translate to a detection limit of about 4×10^{11} atm-cm⁻³ allowing for what appears to be a "memory" signal most likely arising from the high arsenic concentration sample previously analyzed for instrument tuning purposes. Recall that boron exhibited this same kind of memory background even for ¹⁰B. We consistently seemed to be limited to about five decades in dynamic range from the highest doping concentration to the element-specific background detection limit. This observation has dramatic consequences in terms of the ultimate instrument configuration for ultra-trace AB/SIMS work with semiconductor materials. We will discuss these consequences in the next section.

The sample alleged to have an antimony concentration of 1×10^{14} atm-cm⁻³ gives an ¹²¹Sb⁺⁶ signal some 20 times our arbitrary cosmic radiation background of 0.1 cps. Furthermore, we have already noted a 20-fold loss in Sb signal resulting from the foil stripping process necessitated by inadequate field strength in the high energy magnets. With no additional optimization other than improving these magnets we can extrapolate an antimony detection limit to something on the order of 5×10^{11} atm-cm⁻³. Additional optimization may be achieved by investigating other injected species (e.g., SbSi⁻) increased sputtering rate and/or acceptance area of the source mass spectrometer, improved charge state selection at the terminal or even longer counting times. Another factor of 50 (1×10^{10} atm-cm⁻³) appears totally feasible for antimony.

In all three cases, boron, arsenic and antimony, only data for the most favorable analytical approach are included in Figure 8, forming the basis for the above calculations for each element. Two different types of detection limits can be stated, one extrapolated to an equivalent concentration at 0.1 cps as we have done, or another predicated on the minimum "background"

observed for the most favorable species based on float zone silicon regardless of possible background origin. In every instance, background limited detection is inferior to the extrapolated count rate detection limit by several orders of magnitude. Actual realization of the extrapolated values would require elimination of the background by some means. Better source cleaning and/or modifications to the ion source design could be the key steps in this process.

V. Discussion

As might be expected, the results of this preliminary investigation are both encouraging and disappointing at the same time. We are encouraged by the fact that in at least a few isolated cases (arsenic and antimony in particular) some improvement in actual measured detection limits were achieved with little effort expended on optimization, technique development or statistical refinement. If we draw a parallel between AB/SIMS and conventional SIMS using the Cameca IMS-3f, current "state-of-the-art" detection limits (Table 1) in many instances were not immediately realizable when the instrument was first delivered to our laboratory over six years ago. They have evolved with time as the result of major instrumental modifications and a better understanding of the analytical process and instrument on almost an element by element and matrix by matrix basis. Moreover, if we make the comparison between the IMS-3f and its predecessor instrument, the IMS-300, the improvement is much more dramatic. The AB/SIMS instrument at the University of Toronto (and most likely the one at the University of Arizona) are like the Cameca IMS-300 ten years ago, viz. state-of-the-art instruments with substantial room for improvement in design and implementation. The latter observation was our main disappointment, i.e., that the instrument and technique are no more advanced than they appear to be. Major improvements could be made in the ion source and low energy mass spectrometer, high energy filtering magnets, final ion detection and beam diagnostics. The latter are absolutely essential at various strategic locations along the ion optical path for instrument tuning and unambiguous identification of observed signals. It is noteworthy that the Toronto staff have been developing a time-of-flight detection system (isochronator) which, if successful, will constitute a significant improvement in the high energy end of the machine. The low energy end remains an enigma requiring major redesign for multielement survey work at ultra-trace impurity concentrations.

Encouraging, too, are the extrapolated detection limits for arsenic, antimony, phosphorus (from the TI report) and even boron. We seem to have been limited by real elemental backgrounds most likely arising from memory effects of

samples previously sputtered in the source, or from sputtering the high doping concentration specimens used to generate pilot beams for instrument tuning. With the Cameca IMS-3f, we find that we are limited to approximately five orders of magnitude dynamic range (highest to lowest detected signal as in an ion implant depth profile). We attribute this phenomenon to backspattering contamination onto the sample from the planar extraction electrode 5 mm away or possibly stray ions from the sputter crater wall. Thus, if we use a 1×10^{19} atm-cm⁻³ bulk-doped specimen for tuning the AB/SIMS instrument in its present configuration, we will be background limited to about 1×10^{14} atm-cm⁻³ by the source memory effect. One could imagine a number of ways of circumventing the problem from the "brute force" approach of using multiple ion sources, one restricted to only "pure" materials, to a careful (and clever) redesign of the sample holder and extraction optics. This is a situation, however, where the brute force approach is guaranteed to work and has other potential advantages as well.

The limitations arising from our inability to produce and detect negative ions from elements with unfavorable electron affinities can be circumvented using the charge exchange concept the Toronto staff have demonstrated in their ²⁶Al studies and/or optimization of negative molecular ion formation (e.g., FeO⁻ or FeSi⁻). To cover all possible eventualities, one would envision having three different ion sources on the instrument: 1) a conventional Cs⁺ sputtering source essentially dedicated to low impurity level specimens, 2) an ion source employing O₂⁺ or I⁺ for the production of positive secondary ions with a charge exchange canal for negative ion conversion of inherently electropositive species and 3) a pilot beam source (e.g., a glow discharge) from which intense beams of virtually any species could be generated for the purpose of instrument tuning. The present configuration of the Toronto instrument includes two of the three sources, one of which (I⁺ sputtering and charge exchange) was unavailable to us at the time of our experiments.

VI. Conclusions and Recommendations

It seems very clear from the data obtained in this study and other general observations made regarding the AB/SIMS technique and the hardware utilized by the Isotrace Laboratory that ultra-trace bulk impurity analysis significantly surpassing current state-of-the-art capabilities is scientifically feasible. However, existing machines built for the primary purpose of ¹⁴C analysis are ill-suited to survey work with periodic table coverage. Problems exist with both the low energy mass spectrometer and ion optics, and the high energy spectroscopy and detection systems. Again, they are adequate for ¹⁴C but fall short when dealing with common problematic situations in semiconductor

materials like phosphorus in silicon or heavy elements in any matrix. The major reason these machines are configured as they are is that they were intended for ^{14}C analysis at minimum cost. Implementing an accelerator-based SIMS system for optimum operation across the periodic table will be a somewhat expensive proposition (compared to buying a Cameca IMS-3f ion microanalyzer) but imminently within reach of existing technology. Without a detailed cost accounting we would estimate hardware expenses to be about 2.0 million dollars with a first year operating budget for design and construction of 1.0 million dollars. Follow-on funding requirements would be reduced to about 0.7 million dollars annually once the major capital expenditures are made, allowing for full utilization of the facility upon completion.

We would propose to address the low energy end problems in a very straightforward way, viz. replace the single focusing magnet system with a Cameca IMS-3f, or the mass spectrometer employed in the VG9000 glow discharge instrument. Interfacing would involve coupling the mass spectrometer both ion optically and mechanically to a standard 1.7 MeV GIC tandem accelerator, not a particularly difficult task. A simple discharge source would also be needed to generate pilot beams, and a charge exchange canal would have to be included on the exit side of the source for analyzing electropositive species which do not form an abundant negative ion during Cs^+ ion sputtering. A complete redesign of the high energy spectroscopy and detection systems would be absolutely essential including the addition of an isochronator detector similar to the one being designed and built at the University of Toronto. Both the high energy ESA and high energy magnets require redesign to optimize transmission and mass/energy resolution of heavy ions including thorium and uranium.

None of these problems is technologically insurmountable. Under the supervision of the right people, all of the redesigns could be accomplished within twelve months after initiation. For example, existing staff at CHARLES EVANS & ASSOCIATES, including Dr. David Reed, Dr. Filippo Radicati, Dr. Ronald Fleming, Dr. Robert Odom and Dr. Sidney Buttrill have extensive instrument design and construction experience and are currently involved to some degree or another with the development of a TOF SIMS instrument. They, along with Mr. John Huneke, presently manager of Cameca SIMS operations at CHARLES EVANS & ASSOCIATES and soon to be in charge of the glow discharge mass spectrometry operation as well, are highly qualified to perform the low energy mass spectrometry design and interfacing work. Mr. Michael Strathman, currently manager of Rutherford backscattering operations and accelerator technology at CHARLES EVANS & ASSOCIATES has had extensive prior experience with energetic ion beam system design and development at the Lawrence Berkeley laboratory of the University of California and earlier at the accelerator laboratory at the

University of Iowa. Heading the total research team would be Dr. Charles A. Evans, Jr. bringing together his breadth of experience in advanced semiconductor materials characterization, Cameca 3f SIMS and advanced ion beam instrumentation.

VII. Justification

Perhaps the most important issue to be addressed in considering the proposition of building a sophisticated accelerator-based SIMS instrument for ultra-trace impurity analysis of semiconductor materials is "why?" The past decade has demonstrated that many technological breakthroughs in advanced semiconductor materials and processes have resulted, at least in part, from improvements in materials characterization, most notably at trace element levels. The whole saga of chromium in gallium arsenide in the late 1970's and early 1980's speaks to this point. Similar progress appears to be taking place in HgCdTe technology although here the problems seem even more sinister due to the complex convoluted role of structural damage on device performance and the fragile nature of the material. Questions involving bulk trace element-analysis of silicon persist to this day despite the maturity of the technology and its widespread use. Thus, we can anticipate that as devices become more complex and geometries continue to shrink to physical limits, trace impurities at levels presently inaccessible by current analytical methodologies may give rise to unresolvable problems. As an example, we were recently approached by a semiconductor crystal growth group at a major DoD contractor with the question: "could CHARLES EVANS & ASSOCIATES perform bulk analysis of phosphorus in poly-silicon at levels below 1×10^{13} atm-cm⁻³?" Unfortunately, the answer had to be "no, not at the present time." The problem remains unsolved! We would anticipate that AB/SIMS, properly and carefully implemented, could provide the analysis required and thereby open a new "window" on semiconductor materials, heretofore totally inaccessible, with potential technological benefit for both military and non-military microelectronics.

However, like conventional SIMS, AB/SIMS is not limited only to semiconductors. Virtually any solid material lends itself to trace elemental analysis by this technique including nuclear, biological, metallurgical, geological or ceramic materials. Obviously, research will be needed for many of these applications, but once the instrument is built, none of this research should be considered "high risk." It is mostly limited to details of sample preparation and operational protocols. To our knowledge, such a facility would be unique in the world, and could be administered as a national center for trace analysis or a mini-national laboratory with priority given to DARPA/DoD

activities and/or contractors. Should the outcome of the endeavor be such that semiconductor technology is dramatically impacted, it could help to bolster U.S. industry in its world-wide competitiveness, as important to National Defense in the modern world as tactical or strategic weapons systems. If these assertions are true (and we believe they are), a "few" million dollars would be a small price to pay for the potential increases that could result in the economic and military strength of the nation in the decades to come.

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APPENDIX C

Evaluation of Evolving Techniques

Excerpt from

Annual Technical Report
p. 12

for Contract #MDA903-83-C-0099

Investigation and Development of
Advanced Surface Microanalysis
Techniques and Methods

for the Reporting Period

April 1, 1983 - March 30, 1984

N.B. This report was prepared in March 1984 and represents the maturity of the techniques and our understanding at that time. An updated version will be prepared and forwarded to DARPA at a later date.

III. Investigation of Techniques For Achieving Trace Level Detection Sensitivities at 0.1 Micrometer Lateral Resolution

The future demands for trace level sensitivity in advanced electronic devices requires surface microanalysis capabilities which can not be achieved by present day SIMS/ion microanalysis. In fact, these demands will not be completely met even if the detection sensitivity enhancements discussed in the previous section are accomplished. The fundamental limitations of the SIMS technique is illustrated by examining the requirements of ppm detection sensitivities with a 0.1 micrometer lateral resolution and at a 100 Angstrom depth resolution. Even with an optimized SIMS assuming 50% ionization and 10% mass spectrometer transmission, not even one single count would be produced from this volume for a ppm (5×10^{16}) component. It is apparent from this observation that what is required in order to achieve a detectable signal at this concentration is total ionization and mass analysis transmission efficiencies approaching 100%. Thus, we are lead to the conclusion that new analytical techniques must be developed and evaluated if we are to realize the sensitivity and detection limits required for future device geometries.

During this study of new microanalytical techniques and discussions with material scientists, device engineers and crystal growers, it became apparent that even before one must worry about lateral microanalysis with 0.1 micron or so resolutions, there must be improvements made in the ability to perform bulk and depth profiling analyses.

1. There is a continuing need in present semiconductor technologies, particularly those using Si for more sensitive, surface specific analysis to examine a breadth of surface contaminants as a result of surface preparation and cleaning procedures.
2. There is a need for improved depth profiling capabilities with better depth resolution. Improvement is required for a host of technologies in silicon, as well as for devices being fabricated from III-V and II-VI compound semiconductors, wherein very thin layers are used as active layers, or superlattice structures are used to provide the necessary electrical performance.
3. There is a need for more sensitive analysis at the bulk impurity level. Silicon crystal growth technology is still plagued by unintentional

impurities as is GaAs, InP, CdTe and HgCdTe. The new materials are highly non-conducting thereby confounding most of the sensitive, bulk analytical techniques, yet need trace element analyses at the 0.1 to 1000 ppm levels.

Thus research for achieving better detection sensitivity can really be broken down into two studies. One is the achievement of improved capabilities for in-depth and bulk analysis with little or no regard for lateral resolutions as long as 0.1 mm to 1 mm resolutions are provided. The second is the need for an improvement in the overall efficiency of signal generation and collection to accompany sub-micron analyses. Thus, it became incumbent upon us to investigate those evolving techniques which will provide improvements in depth resolution, bulk detection limits or may lead to improved microanalytical and submicron lateral resolution capabilities.

The following provides a brief summary of these evolving techniques followed by a short comment as to their relative advantages and disadvantages. This will then be followed by a discussion of the relative analytical merit and a perspective on these techniques, as well as what might be expected if research is pursued in bringing these evolving techniques to bear on current or future materials or device technologies.

DESCRIPTION OF TECHNIQUES

I. Time-of-Flight SIMS

The first method that one can envision for improved detection sensitivity would combine the ability to detect most or all of the different elements contained in a given sample volume, coupled with the maturity and analytical sensitivity of SIMS. A conventional secondary ion mass spectrometer is a point focus, single ion detector. All other ions of potential analytical interest are lost. Thus, if one wishes to analyze ten different elements from a piece of material, one must consume ten unit volumes of that material. There are two approaches to simultaneous, multi-element detection. One is the use of an extended focal-plane mass spectrometer, and the other is time-of-flight mass spectrometry. At the present time there are no focal plane mass spectrometers in commercial production. They are expensive to construct and the necessary detector technology is quite immature. On the other hand, time-of-flight mass spectrometry is fairly mature. Commercial instruments are available for specific purposes, and the detector technology exists.

In TOF/SIMS, one would use a pulsed primary ion beam of oxygen or cesium ions, depending upon the desired secondary ion species coupled to a time-of-flight mass spectrometer for mass separation and detection. Although one would still achieve only the ion yields available with existing SIMS instrumentation, the value of this technique lies in being able to sample and collect all of the ions produced from a given pulse. Thus in the above example, if time-of-flight capabilities could be implemented, we would be able to detect all ten elements from a single unit volume of material, thereby increasing the effective sensitivity or detection limits of the SIMS technique by a factor of 10. The improvement would be even greater for survey analysis in any materials-limited situation such as the analysis of thin films or micro-areas. Such an enhancement of the multi-element detection capability of the SIMS technique will be necessary when performing survey analyses in submicron areas. The achievement of the submicron capability would be accomplished through the use of a microfocused ion source producing a high current density, pulsed ion beam. There exist high current density, liquid metal ion sources, but they do not seem capable of long-term reliable operation, don't produce a beam of cesium ions and are difficult to pulse. Research in all of these areas is being pursued.

One of the main features of time-of-flight/secondary ion mass spectrometry is that it can be combined with techniques such as resonance or multiphoton ionization for enhancing the conversion of sputtered atoms to ions. Thus, the next generation TOF/SIMS instrument would combine the submicron analytical features of:

1. A liquid metal gun;
2. The ion yields of reactive ion bombardment SIMS or photo-enhanced ionization (resonance or multiphoton ionization);
3. The near 100% collection efficiency of a time-of-flight configuration; and
4. The simultaneous multi-element detection capability of the time-of-flight mass spectrometer.

There are two methods for enhancement of the atom-to-ion conversion process (discussed below), both of which could also be implemented on a time-of-flight SIMS instrument.

II. Resonance Ionization Mass Spectrometry (RIMS)

A variety of workers are currently investigating an evolving analytical technique which employs high power density laser irradiation to bring about the highly specific, highly efficient ionization of a desired atom sputtered into the vacuum. As implemented in present day configurations, the surface of the sample is sputtered using a pulsed ion beam followed by wavelength specific laser irradiation of the sputtered neutral plume so as to bring about a resonance ionization process leading to highly efficient, highly element specific ionization. This process can conceptually provide 100% conversion of atoms into ions and if combined with the proper mass spectrometer could provide near 100% collection efficiency of the ions thereby produced. Between concept and practice lies a host of problems: conceptual, physical and instrumental; which have prevented RIMS from fully achieving its capabilities. However, putting aside current problems, the RIMS technique holds the promise for being one of the most sensitive techniques for analysis of a specific element.

III. Multi-Photon Ionization Mass Spectrometry (MPIMS)

Multi-photon ionization mass spectrometry employs ion beam sputtering, pulsed laser enhanced ionization and mass spectrometry, as does resonance ionization mass spectrometry. However, in the MPIMS technique, one employs a sledgehammer-like approach wherein photons of the highest possible energy or shortest wavelength are brought to bear on the cloud of atoms sputtered by a pulsed primary ion beam. If the photon density is sufficiently high in the sputtered neutral cloud and two or more photons arrive at the same time in the vicinity of a single atom, an electron is promoted from a ground state in that atom into the vacuum thereby producing a positive ion. In this manner, one can produce a broad elemental coverage by photo ionization rather than specific elemental excitation, as does resonance ionization. This technique can be employed for multielement excitation as does SIMS and is readily combined with a time-of-flight mass spectrometer. Interestingly enough, MPIMS should be as sensitive as resonance ionization for most elements with simultaneous excitation rather than being able to select a single element. The technique is quite new but already holds promise as a sensitive technique for the survey analysis of materials.

Comments on I, II, and III

It is interesting to note that the development of time-of-flight SIMS as originally proposed was to provide multielement detection to enhance the

practical detection limits of submicron SIMS. At that time, we proposed the use of resonance ionization to improve detection limits for the analysis of a specific element. Now with the advent of MPIMS, it is possible that an additional mode of excitation could be brought to bear on microanalyses with an advanced TOF instrument.

The nature of time-of-flight SIMS demands the use of a pulsed ion production process so as to bring about the production of the ions in a very short time such that they are able to separate in time without a confusion of masses brought about by a long time of excitation. In the case of the two laser excited techniques, one must employ pulsed lasers to achieve the power densities necessary to bring about the desired saturation of the ionization process in order for these techniques to be truly competitive with conventional SIMS. Thus, in our letter of April, 1984, we requested a redirection of effort in order to bring forward the development of a time-of-flight/secondary ion mass spectrometer. We requested this, not only because of the unique capabilities offered by the TOF/SIMS instrumental configuration, but also because it provides a unique ion optical, analytical bench for next generation instrumentation. As originally proposed, the time-of-flight SIMS process is ideally suited to submicron ion probing for the survey analysis or multielement analysis of specific, localized areas. Independent of the use of a finely focused probe or a broad area analytical ion probe, such a time-of-flight secondary ion mass spectrometer is concomitant to the concepts of resonance ionization or multiphoton ionization mass spectrometry. For this reason, we are convinced that by implementing this TOF/SIMS capability, we will be able to redirect the efforts of this contract so as to bring about the development of new instrumentation of central importance to materials characterization.

An important concept which evolves from the above discussions is that sputtering is a highly effective process for controllably removing atoms from a material and presenting them to an external method for excitation or ionization prior to mass spectrometry. Control of the position, size and rate of removal of the sputtered area provides the lateral and in-depth resolution required for a particular analysis. The ionization process accompanies the sputtering process in conventional SIMS. In the proposed TOF/SIMS configuration, control of ionization and sputtering is intertwined. For resonance and multiphoton ionization (as well as some of the techniques to be discussed below), the "sampling" and "excitation" processes can be separated and individually optimized to the needs of a particular analytical situation.

This theme of ion beam sputtering to sample the material of interest followed by subsequent ionization processes for improvement of the signal-to-noise

ratio will be discussed with the following techniques. In the first technique the focus is on reducing the spectral interference background to improve signal-to-noise, while in the other two, emphasis is placed on increasing the signal.

IV. Accelerator-based Secondary Ion Mass Spectrometry (AB/SIMS)

As is widely known and discussed, the spectral interference due to molecular ions is the most severe problem limiting the intrinsic sensitivity of secondary ion mass spectrometry today. RIMS and MPIMS concepts are attempts to accomplish a reduction in the background produced by molecular ions and/or increase the analytical ion intensity, in order to achieve an improved signal-to-background ratio and hence improved detection limits for techniques employing sputtering. Based on an examination of the mechanisms of secondary ion or sputtered ion production, we believe that there is little that can be done to improve the efficiency of the ionization which occurs during the sputtering process. However, we feel that near-term efforts can be made to achieve a reduction in the spectral background encountered in conventional SIMS. Thus, we proposed and are studying the possibility of reducing the incidence of molecular ions and consequent spectral background through the use of laser oriented processes or MeV accelerator-based secondary ion mass spectrometry. Accelerator-based SIMS involves accelerating negative atomic and molecular ions to MeV energies and directing them through a "semi-dense" material or gas which dissociates molecular species and positively ionizes all of the atomic and collisionally dissociated molecular species. Thus, accelerator-based SIMS as well as laser based dissociation techniques can be regarded as techniques which invoke sputtering and ionization followed by some secondary, albeit non-ionization, process. In this case the secondary process is not to improve ionization efficiency but to reduce the background, given the atomic and molecular ionization processes which accompany sputtering. At the present time, we believe that the ionization processes involved in commercial SIMS instrumentation offers the best sensitivity for much of the periodic table. Only a few elements suffer due to a lack of ionization efficiency, while most limitations can be attributed to spectral interferences. Thus, this emphasis on the reduction of spectral interferences could bring the most benefit in the shortest time.

V. Sputtered Neutral Mass Spectrometry (SNMS)

If we are to pursue the concepts of ionization subsequent to the sputtering process, there are two mechanisms that we can examine, both of which employ the use of plasmas rather than laser based photo ionization as is the case

with resonance and multiphoton ionization. The best understood of these non-laser processes is referred to as sputtered neutral mass spectrometry (SNMS) developed by Professor Oechsner at the University of Kaiserslautern, West Germany. Although Professor Oechsner has devoted most of his time to understanding the fundamental plasma processes involved, we feel the technique of sputtered neutral mass spectrometry provides the potential base for an excellent method to characterize materials important in semiconductor technology. In the SNMS technique, one employs ion bombardment in order to sputter-eject atoms from the material of interest into the vacuum. Thus, one obtains a flux of neutral atoms directed into a plasma chamber consisting of a cyclotron plasma operating on a low pressure of argon. The nature of the plasma is such that approximately 1% of the neutral atoms which enter the plasma become positively ionized by electron impact but do not undergo any hard sphere collisions with the low pressure argon atoms or ions. The ions produced in this cyclotron plasma are then directed into a mass spectrometer for detection. Given that this technique is implemented in the large area depth profiling mode, we can achieve certain very unique analytical capabilities. First, the bombarding ion beam can be of very low energy thereby providing good depth resolution. In fact, with proper electrode configurations, the ions from the plasma itself can be directed against the sample surface with energies in the 200 to 500 electron volt regime, thereby providing the optimum in depth resolution. Once the atoms are ejected from the sample surface either by a true ion beam or by the plasma ions, they enter into the plasma for ionization where the "matrix" is the plasma. Thus, we can achieve a reduction in the matrix effect which plagues many analytical techniques. Any process which removes the atom of interest from the matrix before bringing about the analytical excitation can only provide improved quantitative capabilities. Thus, the use of a two step process, available with resonance ionization and multiphoton ionization can also be implemented with sputtered neutral mass spectrometry. The first, sputtering, provides the sampling of the material of interest, while the secondary process, photon bombardment or in this case plasma excitation, provides the generation of the analytical signal in a matrixless environment. Thus, sputtered neutral mass spectrometry appears to provide a quantitative capability heretofore unrealized with any of the other microanalytical techniques. Conceptually, resonance ionization and multiphoton ionization should be quite quantitative, but the only supporting data available is on sputtered neutral mass spectrometry. Based on these conceptual evaluations, CHARLES EVANS & ASSOCIATES has independently prepared a proposal to DARPA under the auspices of the Small Business and Innovative Research Program in order to evaluate and develop sputtered neutral mass spectrometry for quantitative microanalysis.

The following information, developed in conjunction with that proposal preparation, is provided for completeness in this Annual Report.

Throughout our studies of evolving techniques, it has become very obvious to us that the separation of sampling of the material and excitation of the atoms of interest can provide unique capabilities heretofore unavailable. Thus, we feel that sputtered neutral mass spectrometry provides several unique capabilities. First, the use of low energy ion bombardment provides the potential for depth resolutions which are not generally achieved with present profiling techniques. Secondly, the removal of the atom from the matrix prior to excitation provides a matrixless and, hence, highly quantitative capability that has yet to be achieved in any surface or microanalytical technique. Thirdly, the SNMS technique is quite amenable to the use of a finely focused ion beam probe, either DC or pulsed for sampling and the use of an extended focal plane or time-of-flight mass spectrometer for simultaneous detection.

It should be noted that taken in total, the efficiencies of:

1. Sputtered atom introduction into the plasma;
2. Ionization by the plasma; and
3. Collection of the ions exiting the plasma chamber

are sufficiently low that SNMS cannot achieve the detection limits of conventional SIMS, much less be applicable to highly sensitive, submicron analyses.

VI. Glow Discharge Mass Spectrometry (GDMS)

There is presently a new technique for bulk analysis which also employs sputtering for removing atoms followed by secondary excitation in a plasma, glow discharge mass spectrometry (GDMS). During the preparation of our proposal we did not consider this technique since it is truly a bulk analytical technique. However, due to our investigations during the first year of this research activity and the perceived need for improved bulk analytical technique, we propose that the glow discharge mass spectrometer deserves serious consideration as an advanced materials analysis technique. Over the past several years, a few investigators have employed glow discharges for excitation of impurities contained in a material. Basically, one places the sample in a DC plasma containing argon ions which sputter the surface of that material into the gas phase. In the DC glow discharge, electron impact

and Penning ionization produces ions of the sputtered neutrals. The ions produced by the glow discharge are then introduced into a mass spectrometer for mass separation and detection. This technique has the potential for providing part per billion (ppb) detection limits in a bulk analytical mode. One obtains a pseudo-depth profile since the material is sampled via the sputtering process which erodes successively deeper layers of the material prior to ionization in the plasma. This technique appears to provide state of the art bulk analysis, much as spark source mass spectrometry did 20 years ago, but instead of using photographic plates with their extended processing times, one can use quantitative pulse counting with 10 to 20 minutes required to analyze up to 20 different elements in a given sample. We are presently giving serious consideration to and are presently evaluating GDMS for bulk analysis. Given the nature of the analytical process wherein sampling is provided by sputtering and ionization provided in a separate step we feel GDMS could be eventually molded into a technique to provide large area depth profiling with excellent sensitivities and depth resolutions.

COMPARISON OF EVOLVING ANALYTICAL TECHNIQUES

With this host of new analytical techniques, none of which have any tried and true capability as do the existing techniques of SIMS, Auger electron spectrometry and Rutherford Backscattering spectrometry, how does one determine the best place to put one's efforts? We offer the following as a perspective on the evolving techniques discussed above.

1. Secondary Ion Mass Spectrometry (SIMS) (We are including this technique as the existing, mature, analytical approach)
2. Time-of-Flight SIMS
3. Accelerator-based SIMS
4. Resonance Ionization Mass Spectrometry
5. Multiphoton Ionization Mass Spectrometry
6. Sputtered Neutral Mass Spectrometry
7. Glow Discharge Mass Spectrometry

The topics to be discussed for this intercomparison will be:

- I. The mechanism of the ionization process at our level of understanding and how the mechanism relates to the ability of the technique to quantitated;
- II. Quantitation;
- III. Uniformity of ionization;
- IV. Spectral features and spectral interferences
- V. Sensitivity of the technique which will be discussed as:
 - A. The ionization efficiency or ion yield;
 - B. The volume sampled during the analysis; and
 - C. The extraction and transmission efficiencies of the ion source/mass spectrometer combination.
- VI. The lateral resolution capabilities;
- VII. Depth profiling capabilities, in particular the depth resolution that should be attainable; and
- VIII. Outermost monolayer or surface sensitivity.

The first thing to note about all of these techniques is that they are all using mass spectrometric analysis and detection. That is to say:

1. The techniques are all capable of providing full periodic table coverage from H to U, and beyond;
2. They all provide isotopic detection capability;
3. They are not plagued by either detector noise or broad spectral backgrounds as one has with optical techniques. It is interesting to note that although resonance ionization is practiced using mass spectrometry, it need not have a mass spectrometer since one should be able to provide the necessary elemental specificity by choosing the appropriate laser wavelength and detecting the ions of only the one element that are produced. However, given the level of maturity of the technique, it is incumbent upon a responsible user to employ a mass spectrometer as a detector to insure that there are not broad band secondary ionization processes taking place which would provide ions of molecular species or another element which would give erroneous results.

4. They are operated in a regime where single ion counting can be employed.

I. Mechanisms of Ionization. There is a basic difference between SIMS, time-of-flight SIMS and accelerator-based SIMS, and the other evolving techniques. In the SIMS techniques, the ionization process accompanies the sputtering event; therefore, we do not have the opportunity to independently control the ionization process beyond the use of reactive ion bombardment with O or Cs ions for optimized ionization. At this time, the exact nature of the ion production process, either positive or negative ionization, is not well understood. The nature of the ionization process and its exponential dependence on the ionization potential or electron affinity provides very large variation in the ion yields. For elements with low ionization potentials (K, Na, Li) or a favorable electron affinity (Se and Te) we have very high ion yields approaching a 10 to 50% efficiency of conversion of sputtered atoms into secondary ions. Alternatively, for those species with very high ionization potentials and unfavorable electron affinities (Zn, Cd and Hg being the classic examples), we have some four or five orders of magnitude lower ionization efficiency. Needless to say, the lack of understanding of the ionization process and the broad variation in ion yields leads to difficulties in quantitation and large variation in the relative sensitivities of elements that might be analyzed.

Of the remaining techniques of resonance ionization, multiphoton ionization, sputtered neutral mass spectrometry and glow discharge mass spectrometry, all employ ionization mechanisms which occur after the sputtering event and can be considered to occur separated in time as well as in space. As discussed above, both resonance ionization and multiphoton ionization employ laser irradiation to bring about a post sputtering photo ionization process. In resonance ionization one must bring in at least one if not two laser beams of a specific wavelength to bring about the selectivity fundamental to resonance ionization. Thus, at least theoretically, ionization of a single element or even a single isotope can be accomplished, and all the other sputtered species are not ionized and thus do not complicate the analysis. In multiphoton ionization one uses a brute force method employing very short photon wavelength, (250 nanometers or less), to bring about non-specific multiphoton absorption by all the sputtered atoms. The power density is such that two or more photons arrive in the same position in space and time, in order to bring about the ionization. In the case of resonance ionization, there is essentially 100% ionization of the atoms of interest present in the volume defined by the laser beam and the sputtered neutral atom plume. Atoms present outside that volume are not ionized. In the case of multiphoton ionization there is a 100% ionization of most of the atoms present in that volume defined by the laser and the sputtered neutral plume. However, if an atom with a

sufficiently high ionization potential is present, there may be an insufficient number of photons to provide enough energy to bring about a 100% ionization. For example, if we employ 3eV photons and must examine an element with an ionization potential of 10eV, then at least 4 photons must be present within a very short time at each atom; if not, then there will be no ionization. Of the other two techniques involving auxiliary or post-ionization, SNMS and GDMS, both employ a plasma or plasmalike process to bring about the ionization. For sputtered neutral mass spectrometry, the sputtered atoms are introduced into a low energy, low pressure plasma where approximately 1% of the atoms that enter the plasma are ionized by electron impact mechanisms. There is a small but measurable variation in the ionization efficiency (a factor of 10) across the periodic table. Although this sounds quite large, remember that with SIMS there is a 10^3 to 10^5 variation in sensitivity or ionization efficiency. Moreover, the variation in SNMS ion yield from element to element is constant, and the ion yield for a given element is constant or reproducible. Thus, the number of ions produced per atom of a given element traversing the plasma is always constant, i.e., the conversion or relative sensitivity factor for a given element is independent of the matrix from whence it came. Thus, a standard of boron in silicon could be used to quantitate the analyses of boron in GaAs, steel, etc. Glow discharge mass spectrometry is similar to SNMS, in that the sputtered atoms are introduced into a plasma, a glow discharge in this case, wherein there is ionization by electron impact as well as Penning ionization. Although the exact nature of the ionization is not well understood as well as in the other post ionization techniques, the ionization efficiency is good and most importantly the uniformity of the ionization from element to element is excellent. The most important aspect of these four auxiliary ionization techniques is that the ionization takes place external to the sample or matrix and in a region of somewhat uniform composition. In the photo ionization techniques the vacuum acts as the matrix, while with sputtered neutral mass spectrometry and glow discharge mass spectrometry, the argon based plasma is the matrix.

II. Quantitation. In order to quantitate a mass spectrometric technique (as with any analytical technique), one must convert the measured ion intensity from counts per second or amperes per second into concentration. With almost any analytical technique, one employs either:

1. Standards wherein the conversion factor is calculated from samples containing known concentrations and measured ion intensities or;
2. An empirical method for calculating the sensitivity factor based on first principles. For a variety of reasons we propose that one must

employ standards. In the case of these techniques, all employing sputtering, we must know several factors in order to quantitate:

- a. The number of atoms sputtered from the sample per unit time;
- b. The conversion efficiency of atoms into ions or the ion yield;
- c. The number of ions extracted from the ionization volume into the mass spectrometer (the extraction efficiency);
- d. The transmission efficiency of the mass spectrometer; and
- e. The detection efficiency or quantum efficiency at the detector.

Determining these from first principles and keeping them constant over a long period of time would be difficult, if not impossible. Thus, in all cases, we must use some sort of standardization process. It is important to remember that the ion yields can vary not only from element to element but from one material to another, i.e., the matrix effects. Matrix effects are processes taking place during ionization which lead either to a nonlinear relationship between ion intensity and concentration or change the ion intensity produced for a given element when changing from one matrix to another. That is to say, B in Si may well have a different ion yield than B in GaAs. In light of these concepts, let us now examine the quantitative aspects of the evolving techniques. As is implied by the previous discussion secondary ion mass spectrometry (conventional, TOF and accelerator-based) requires the use of standards in order to accurately convert ion intensity into concentration. Since the ionization efficiency varies by large amounts from element to element, one can not merely ratio the intensity of two elements in order to obtain a concentration ratio. Moreover, since the ionization takes place in or near the surface of the sample (matrix), SIMS is susceptible to matrix effects which can produce a different ion yield for given element from one matrix to another. Thus standardization is imperative. Given that one has standards which very accurately mimic the unknown in composition at the matrix level, then quantitation can be good to excellent. For instance, if a given B implant is analyzed 5 or 10 times, standard deviations of better than 5% can be obtained. The same is true at major constituent levels, as we have shown in the above discussion of BPSG quantitation using externally generated standards. The real difficulties in quantitating SIMS come in trying to determine the relative concentrations of two elements in the same material for which there are no standards or for quantitating impurities in a matrix for which no standards are available.

Although the variation in ionization efficiency is not as great for the four post ionization techniques as it is for SIMS, many of the same basic considerations are required for quantitation. That is to say, how do I convert the number of ions detected into a concentration in the matrix of interest? Of course, the techniques of resonance ionization, multiphoton ionization, sputtered neutral mass spectrometry and glow discharge mass spectrometry are all amenable to quantitation using standards. However, if the mechanisms of ionization are as proposed and one is able to control the sputtering process or at least understand the sputtering process, one should be able to go beyond the requirement for standards and begin to perform semiquantitative analysis without a standard. Certainly this is possible by multiphoton ionization, sputtered neutral mass spectrometry, glow discharge mass spectrometry and probably multiphoton ionization as shown by the workers in these three areas. In these cases, one is bringing about the ionization of all of the species sputtered from the sample, either with the laser as in MPIMS or by the plasma in SNMS and GDMS. Since these techniques show a fairly uniform excitation across the periodic table (i.e., across ionization potentials), then one should only need to take the intensity of any element, divide it by the sum of the intensity of all the elements to obtain a semiquantitative analysis. In a material with a single major constituent one merely takes the intensity of an impurity, divides it by the intensity of the matrix ion (after correction for isotopic abundances) to obtain a semiquantitative measure of the concentration of that species in that matrix.

The phenomenon central to this semiquantitative approach is the external or post sputtering ionization processes involved in these techniques. For example, the success of this approach has been shown by the one group using glow discharge mass spectrometry. In the case of a copper matrix, they found no more than about a 15% change in ionization efficiency or sensitivity across an approximately three electron volt variation in ionization potential. As was said earlier, the sputtered neutral mass spectrometry technique has demonstrated uniform ionization to within a factor of 3 to 10. With the multiphoton ionization technique so immature, we can only draw a conceptual conclusion.

Resonance ionization, on the other hand, is in a way caught between the difficulties of SIMS and the theoretical ability to quantitate from first principles. If one assumes that all of the parameters influencing the introduction of neutral species into the ionizing volume (the sputtering process) and the if extraction and transmission efficiency of the mass spectrometer stay constant, then one could assume 100% ionization for any element under study and arrive at a concentration. Unfortunately, there are

nuances of the resonance ionization process that are rarely taken into consideration:

1. The sputtering rate of a given material controls the rate of ejection of the neutral atom of choice which yields the detected ion intensity. Thus, without a knowledge of the rate or volume of matrix removal, how is the assumption of 100% ionization converted into a concentration?
2. The solid angle of emission and hence the number of neutral atoms subtended by the laser beam can vary due to crystallographic effects and from material to material.

The specificity of the resonance ionization process may be so great as to excite only those atoms present as ground state neutrals and ignore those atoms emitted as excited neutrals, positive or negative ions or as molecular species. Thus the excitable atom pool is dependent on the secondary ions formed and the variation in molecular species formed. Some of the problems could be mitigated by monitoring the intensity of a matrix ion. However, the technique of ionization is so specific, a two ionization process (one laser-photon process exciting the impurity of interest and the other exciting the matrix of interest) would be necessary. This would seem to be quite expensive.

III. Uniformity of Ionization. Having discussed the mechanism of ionization and quantitation, we have basically addressed the uniformity issue. Given data that exists to date, we would say that glow discharge mass spectrometry has the most uniform ionization followed by sputtered neutral mass spectrometry. We have seen no data which speaks to the uniformity of ionization of different impurities and different matrices for multiphoton and resonance ionization. From first principles, we would argue that they are next in line from a uniformity standpoint, followed by conventional and TOF SIMS, and accelerator-based SIMS would be the worst.

IV. Spectral Features and Spectral Interferences. As with any analytical technique employing spectroscopy, be it optical or mass, we must be concerned about the nature of the spectrum and the backgrounds present, and the consequent impact on signal to background, sensitivity, and attainable detection limits. Mass spectrometry rarely has any continuum spectral features as are commonly encountered in optical spectroscopy. Mass spectrometry can have one of three kinds of spectral interferences:

1. Isobars are isotopes of two different elements having masses sufficiently close together as to be inseparable within conventional resolution.

2. Multiply charged ions are species for which the charge-to-mass ratio cause them to be detected at one-half of their actual mass, where there may be an ion of interest.
3. Lastly, molecular ions are species which result from the association of two or more isotopes which then may fall at a mass of interest.

Thus, any mass spectrometric technique must deal with these spectral features which can result in an undesired signal occurring at the mass of interest. Generally speaking, any technique which is used to reduce the incidence of an interfering species will require the reduction in another analytical feature. Traditionally, the reduction of a spectral interference is obtained by the use of high mass resolution techniques wherein one can resolve the exact mass differences which generally occur between any two ions. The hardest interferences to resolve are isobars since the exact masses may vary by as small as one part in 10^5 or 10^6 . Multiply charged ions are either very difficult to resolve since they act much as isobars or are no problem at all since the doubly charged ions of an odd isotope would occur at a half mass, far away from the mass of interest. In the case of molecular ions, we reach an intermediate resolution requirement wherein mass resolutions of 500 to 10,000 are required to reduce the effect of the molecular species. Secondary ion mass spectrometry produces few multiply charged ions, is rarely plagued by isobars but does encounter a large number of molecular ions. The variety of techniques which are used to reduce these spectral interferences include Voltage Offset and High Mass Resolution (please see the attached application notes which have been generated some years ago by CHARLES EVANS & ASSOCIATES explaining these two modes of operation.)

Time-of-flight SIMS will, of course, be plagued by the same spectral problems as conventional SIMS but would not have the opportunity to use high mass resolution due to the spectral resolutions obtained in a time-of-flight mass spectrometer. Of course, accelerator-based SIMS is founded on reducing the incidence of spectral interferences at low mass resolution and is quite successful. One discriminates against isobars since each of the isobaric species will have a different atomic number or Z and, therefore, will be stripped of its electrons to differing extents in the stripping process and will have a different response in the Z sensitive detectors used by AB/SIMS. These detectors allow discrimination between two elements at the same mass but which have different atomic numbers. Multiply-charged ions are not produced during the negative ion production required of AB/SIMS, and the incidence of variable charged states at the detector end are easily taken care of by the charge and mass spectroscopies used in this technique.

In theory, resonance ionization provides such elemental selectivity in the ionization process that one can select the exact element of choice such that isobaric interferences, doubly charged ions or molecular ions will not be produced. To date there have been reported several instances of broad band excitation or alternate pathways which do lead to the production of undesired ions. However, the incidence of a spectral interference is still very, very small, and this technique probably represents one of the most successful techniques at reducing spectral interferences (accelerator-based SIMS being second most successful). Multiphoton ionization is in a state of infancy, and, although we cannot comment specifically on the processes, multiphoton ionization may well lead to partial reduction of spectral interferences by dissociation of some of the undesired molecular ions. We do know that the second ionization potentials are high, thus there is a low probability of doubly charged ion formation, and the technique will have to deal with isobaric interferences, although their incidence is low in most materials.

Both the sputtered neutral mass spectrometry and glow discharge mass spectrometry employ a sufficiently low energy of ionization that multiply charged ions are rarely encountered and isobarics must be dealt with as with any mass spectrometry technique. Again, due to the infancy of the techniques, conclusions on the impact of molecular ions are difficult. In sputtered neutral mass spectrometry singly charged molecular ions are observed, but their incidence seems to be quite low. In glow discharge mass spectrometry, the pressure in the plasma is quite high, and we feel that there is a sufficient amount of dissociation of molecular species that the incidence of molecular ions is very low. Based on the limited amount of data, glow discharge mass spectrometry would seem to show a low incidence of spectral interferences because the ionization is fairly gentle, producing very low kinetic energy ions, hence, there is ample opportunity for using high mass resolution. To date, the technique has shown the ability to operate with sub part per million detection limits while operating in the high mass resolution mode in the presence of severe multiply charged and molecular ion interferences.

V. Ultimate Sensitivity. Sensitivity can be defined in several ways. Sensitivity can be the overall efficiency of the measurement process, i.e. the number of ions detected per atom in the sample, or it can be the absolute detection limits in ppm or ppb. The ultimate sensitivity of the techniques can be influenced by several features which can only be partially deconvoluted. The ultimate sensitivity of any of these techniques is the product of many factors. If we think in terms of detection limits being determined by the intensity of the element of interest (in the absence of a spectral interference, then):

Although all of these factors can strongly influence the attainable detection limits, there are two which most significantly differentiate the techniques under discussion:

1. The numbers of atoms sputtered per second since this parameter affects the number of atoms available for signal generation; and
2. The number of ions produced per atom sputtered since this step is potentially the most limiting step in the generation of analytical signal from the sputtered atoms.

To a lesser degree, the collection efficiency of the mass spectrometer optics is also highly controlling. The nature of the ionization process, and the angular and energy divergence of the ionization process, the angular and energy acceptance of the mass spectrometer are central in the matching of the emission characteristics of the ion source and the efficiency of acceptance by the mass spectrometer. The following discussion will comment on those aspects of each technique which are critical.

The number of atoms sputtered per second represents the results of a variety of physical and instrumental parameters such as the area sputtered (microanalytical versus macro- or bulk analytical) and the linear rate of removal (angstroms/sec). In the case of the pulsed sputtering techniques (TOF/SIMS, RIMS and MPIMS) the linear rate of removal can be quite low due to short "on" time (10-100ns) and the low repetition rate (10^3 for TOF/SIMS and 10 to 30 per second for RIMS and MPIMS). On the other hand, the sputtering rate and the area sputtered can be very large for the bulk or large area profiling techniques of AB/SIMS, SNMS and GDMS.

The ionization efficiency is the ability to convert a sputtered atom into an ion and is one of the most critical issues in determining the overall sensitivity of a technique. In conventional SIMS the combination of reactive ion bombardment and the analysis of species with moderate to low ionization potentials (less than or equal to 9eV) or moderate to high electron affinities (greater than or equal to 1eV), the secondary ion yield can be of the order of 1 to 50%. When operated at low mass resolution, the collection and transmission efficiency of an optimized secondary ion mass spectrometer (i.e., the Cameca IMS-3f) can be 10 to 50% depending on the exact operating conditions. Thus, for a significant number of the elements in the periodic table, one ion per hundred to one ion per thousand atoms sputtered can be detected. For time-of-flight SIMS we can expect the same ion yields and perhaps even higher extraction efficiency. Additionally, TOF/SIMS offers the efficiency of SIMS coupled with the ability to detect all masses sputtered

from a given volume of material, thereby improving the effective detection limits by at least a factor of ten.

Both resonance ionization and multiphoton ionization mass spectrometry tend to have very high ionization efficiencies for the atoms sputtered from the sample which are in the volume defined by the laser beam and the sputtered neutral plume. Any species falling outside this region are not ionized. For RIMS the ionized ratio is said to be 5 to 10%, and an estimate for multiphoton ionization would be 1 to 10%. Moreover, for both of these techniques (and for TOF/SIMS, to a lesser degree), the volume of material sputtered per unit time is exceedingly small due to the low duty cycle of the pulsed ion source and the pulsed lasers. The collection and transmission efficiencies can vary depending on the mass spectrometer design. Resonance ionization is much like conventional SIMS and AB/SIMS, in that the mass spectrometers presently in use detect only one mass at any given instant, therefore, losing the data produced at all other masses. Multiphoton ionization is at present implemented on a time-of-flight system, combining the high ionization efficiencies of the multiphoton ionization process with the high transmission and simultaneous or multielement detection of the time-of-flight mass spectrometer. From the previous discussion, it becomes clear that one could practice RIMS or MPIMS on a TOF/SIMS with the addition of some timing electronics and the appropriate laser or lasers. Hence, our proposal to begin the design, assembly and testing of a TOF/SIMS.

The necessary use of a tandem accelerator for accelerator-based SIMS requires the use of Cs ion bombardment and negative ion spectroscopy SIMS. This is fine for those electronegative species that form negative ions with a high efficiency. In the case of the electropositive elements for which one conventionally employs oxygen ion bombardment, techniques have been developed for enhancing the production of negative ions containing the element of interest. Generally this is accomplished by flooding the Cs bombarded surface with oxygen to produce molecular species with a high electron affinity which are then dissociated in the stripper step in order to provide the atomic ion of interest. The mass spectrometers employed for accelerator-based SIMS are low resolution, high ion transmission systems, thus we have fairly good ion collection and transmission through the system. The detectors are based on pulse counting techniques and therefore give very high detection sensitivities. Thus, the sensitivity of accelerator-based SIMS is quite good, and it has yet to be fully assessed as to its true quantitative ability.

Sputtered neutral mass spectrometry provides ionization efficiency of about 1% of the atoms sputtered from the sample which traverse the ionizing plasma. The proportion of atoms introduced into the plasma in this technique has yet

to be assessed. Depending upon the mass resolutions required, sputtered neutral mass spectrometry should be capable of transmissions approaching that of a conventional SIMS under the same mass resolution conditions. Thus, the technique is almost certainly capable of sub-ppm detection limits. Glow discharge mass spectrometry consumes material at a very high rate since sputtering occurs on a broad front, thereby providing a very high rate of introduction of species into the ionizing volume, but the high ionization efficiency on the ionizing plasma has yet to be assessed. The coupling of reasonable extraction efficiency and high transmission mass spectrometry leads to very good detection limits for this technique. The technique has already exhibited bulk analysis sensitivities on the order of 1 to 10 parts per billion, and the technique is only evolving. At the present, the GDMS technique seems most suited to trace element bulk analysis.

VI. Lateral Resolution. The next analytical feature to be discussed is that of lateral resolution, which governs the ability to obtain an analysis of a specific localized area or to provide an ion image depicting maps or pictures representative of the relative distribution of a given isotope or element. There are two instrumental ways to achieve ion images. One is through microprobing techniques, wherein a microfocused source of excitation is brought to bear on the region of analytical interest. An ion image is generated by rastering that excitation about the sample surface so as to sequentially sputter microscopic areas on the sample and then use the mass spectrometer output to modulate the intensity axis of an oscilloscope which is synchronously rastered with this exciting beam. The alternative approach is to use ion microscope techniques wherein specialized ion optics are used to extract an ion image of the sputtered ions while maintaining the relative position of the ions as they are emitted from the surface. Thus, in a ion microprobe, one generates the picture points or pixels of the ion image sequentially much as a TV screen generates an image sequentially. Alternatively, the ion microscope generates picture elements from all areas on the surface of the sample simultaneously much as an optical microscope provides a light image of the surface of the material. For a variety of reasons which are beyond the scope of this report, the ion microscope technique is the best way to provide ion imaging, and it also provides the best "all around" depth profiling capabilities. However, it does suffer from the difficulties in localizing the analysis to a small portion of a sample, as can easily be done with microprobe techniques.

Conventional secondary ion mass spectrometry can be practiced either in an ion microprobe or ion microscope mode of analysis. Commercial instruments are available for both modes of operation, but the most developed technology and most broadly used instrument happens to be an ion microscope (the CAMECA Ion

Microanalyzer). The lateral resolution capabilities of the ion microprobe and ion microscope can be easily considered microanalytical. Ion microscope instrumentation, as presently conceived, provides lateral resolutions of the order of 0.3 to 0.5 microns on well behaved samples. At the present time, commercial ion microprobes are capable of lateral resolutions using a beam focused to the order of 2 to 5 micrometers. Thus the present ion microscope instrumentation provides much better lateral resolution. At the present time, one can envision improvements on the incremental front to the lateral resolution to the ion microscope, bringing its resolutions to the order of 0.1 to 0.25 micrometer. Lateral resolutions with the ion microprobe can be dramatically improved through the use of high intensity liquid metal ion sources. These liquid metal ion sources should provide lateral resolutions of the order of 0.1 to 0.2 micrometer if implemented on conventional SIMS instrumentation. As was discussed in the proposal which resulted in this contract, the number of atoms available for an analysis is governed by the area of the analysis, all other things being equal. Thus, if we were to implement microanalysis at the submicrometer level, a host of other instrumental advances will have to be accomplished in order to maintain the desired sensitivities. If this is to be done with ion microscope instrumentation, we will have to develop the ability to laterally discern or depict the area of ion emission quantitatively. Such is the idea for the use of digital imaging processing, which we are implementing under another contract. An alternative approach is the use of the liquid metal ion source for an ion microprobe based analysis. If submicrometer capabilities are to be obtained with the ion microprobe, reliable, long term metal ion sources must be developed. This process is being pursued by several government and privately funded research efforts. One of these efforts is our subcontract under the auspices of this grant to the Oregon Graduate Center for development of a liquid metal ion source.

We feel that the second most important consideration for achieving a viable analysis from submicron lateral resolution capabilities is the implementation of parallel ion detection of all the ions produced during a given sputtering event so as to efficiently utilize the data that is made available during a microanalysis. This is the basis for our recommendation and proposal to develop a time-of-flight spectrometer in anticipation of attaining submicron lateral resolutions with good elemental coverage. We should note that parallel ion detection can be achieved with a focal plane mass spectrometer, however, such instrumentation is not commercially available and would be very expensive to design and implement and is not within the budgetary scope of this contract. Moreover, time-of-flight SIMS is easily combinable with the pulsed laser requirements of multiphoton ionization, as well as resonance ionization techniques.

As implied by the previous discussion, submicron lateral resolution could be attained with either resonance ionization or multiphoton ionization using ion microprobe concepts, if we can overcome the problems associated with pulsing the submicrometer ion beam. At this time we would be hesitant to say whether one could use ion microscope techniques with these post ionization concepts (RIMS, MPIMS and SNMS) since the energy and angular divergence of the ion beam will be exaggerated by the post ionization process and may lead to problems in stigmatically focussing these ion sources. Lateral resolution capabilities of accelerator-based SIMS are presently nonexistent; that is to say, all the instruments in existence use a 1 mm or larger primary ion beam. However, there is nothing fundamental to prevent the implementation of microfocused ion beams, just as could be done for SIMS, TOF/SIMS, RIMS, MPIMS or SNMS. However, the collisional processes involved in the AB/SIMS stripping process would probably preclude ion microscope methods. Sputtered neutral mass spectrometry, as mentioned above, would be like any of the post ionization techniques (RIMS and MPIMS) in which a liquid metal ion microprobe could be easily employed, but SNMS would probably not be amenable to ion microscope techniques. Given the nature of the glow discharge process, wherein a large area, high pressure plasma contacts and sputters the surface of the sample, we can presently see no possibility for microprobe or microscope imaging. It is possible that sputtered neutral mass spectrometry could be implemented on an ion microscope, but it would face the same difficulties as resonance or multiphoton ionization, i.e., the energy and angular dispersion of the ions and the potential for scrambling of the image prior to the ionization process.

VII. Depth Profiling. The last analytical feature to be discussed is that of the ability of the techniques to provide a depth profile and the potential depth resolutions attainable by each of the techniques. SIMS is already a highly accomplished depth profiling technique providing depth resolutions of the order of a few tens to hundreds of Angstroms or 1% of the depth sputtered, in a well behaved sample. These depth resolutions are accomplished over analytical areas of the order of 150 micrometers in diameter and provide detection limits which range from 10^{13} to 10^{17} at/cm³, depending upon the ion of interest. Conceptually, there is no reason that accelerator-based SIMS, resonance ionization or multiphoton ionization could not provide depth profiles. At the present time the instrumentation does not. Accelerator-based SIMS is still operating in the bulk analysis mode while the present day instrumentation for resonance ionization or multiphoton ionization leads to little or no capability for depth profiling over significant depths due to the low duty cycle for sputtering available from the instrumentation. Sputtered neutral mass spectrometry technique can and does perform depth profiles using either an external ion beam (as does SIMS, RIMS and MPIMS) or by bringing the plasma (also responsible for ionization) in contact with the sample surface in

order to erode the surface in a highly controlled fashion. Since the argon ions from the plasma are initially at a low energy (10 to 20eV), their impact energy can be controlled to be of the order of 100 to 300eV. This is sufficient to bring about the sputtering process but allows for minimal ion beam mixing. At the present time sputtered neutral mass spectrometry probably has the best depth resolution of all of the profiling techniques.

Glow discharge mass spectrometry, as it is presently configured, does not provide for depth profiling in a controlled fashion. Although the sputtering process that is used to introduce the ions into the ionizing plasma sequentially sputters surface layer after surface layer, this is accomplished with no regard for geometry, thereby leading to poor depth resolution albeit a sequential layer removal process.

During this study we have isolated an important analytical requirement. The need to perform a highly sensitive surface analysis for an impurity or impurities of interest, or, more importantly, to provide a full periodic table coverage survey analysis while constraining the analysis to the outermost few monolayers or to a few monolayers about an internal interface. Conventional secondary ion mass spectrometry has the sensitivity to achieve this if one operates under low mass resolution conditions and does an element by element analysis. Inherently, accelerator-based SIMS should provide the same basic surface sensitivities as conventional SIMS, with the added benefit of reduced spectral interferences. Spectral interferences can be somewhat problematic in a surface analysis since there are a host of impurities and environmental contaminants present on the surface which lead to a prodigious number of molecular ions. Time-of-flight SIMS has the potential for providing an exceedingly sensitive survey analysis of the surface of the material. Since it is a pulsed technique, one can change the pulse repetition rate and duty cycle in order to sputter as little or as much of the surface per unit time as might be desired. This controllable sample rate combined with the high ion yields inherent in SIMS and the high transmission capabilities of a time-of-flight SIMS make the parallel detection capabilities of the time-of-flight SIMS highly useful in any multielement or survey analysis.

Resonance ionization, if it lives up to the promise of being the most sensitive of the techniques, would be a very good surface analysis technique in that it is pulsed, and one can control the erosion rate. However, it is severely limited by the need to use a specific wavelength laser combination for each individual element. Thus, one would take hours or days to accomplish a single multielement survey analysis of the surface of the material which the other techniques could accomplish in 15 minutes. Multiphoton ionization, on the other hand, would have very close to the same sensitivities as resonance

ionization; however, it would far exceed resonance ionization in the ability to analyze impurities on the surface due to the broad elemental coverage of the excitation and the use of time-of-flight mass spectrometry for parallel ion detection.

At this point we reach a variety of tradeoffs which requires that we consider the general requirements of a laboratory or a specific analysis. For example, TOF/SIMS and MPIMS have very good to excellent ionization efficiencies, provide parallel detection for multielement or survey analysis but would suffer from spectral interferences. On the other hand accelerator-based SIMS and RIMS would have minimal spectral interferences and would have good to excellent ionization yields but would detect only one mass of the many produced at any given time.

VIII. Proposed Approach. We see the following as the direction we are corporately pursuing and the direction for DARPA consideration. Secondary ion mass spectrometry is a well known, very mature technique and has potentials that are as yet undeveloped. We hope to achieve these through the molecular dissociation aspects being pursued under this contract and to evaluate accelerator-based SIMS as a component of these undeveloped capabilities of SIMS. At the present, glow discharge mass spectrometry seems to be well developed instrumentally but does need applications orientation. Although not within the proposed activities of this contract, we are sufficiently convinced of the viability of glow discharge mass spectrometry that we will probably add a system to our analytical capability by the end of 1984.

On the instrumentation development front, we would propose two parallel activities: one is the development of a time-of-flight SIMS instrument in order to hasten the available of this parallel detection technique combined with its capabilities as a workbench or ion optical bench for the development of multiphoton and resonance ionization techniques. The second is the development and evaluation of sputtered neutral mass spectrometry as a next generation technique for quantitative microanalysis and depth profiling.

Obvious by its omission is an emphasis on resonance ionization concomitant with its reputed potential. At the present time there are four Federal laboratories, one university research group and one Federally funded, private laboratory pursuing RIMS. Until some of the potentials are recognized, the above support and activity seems sufficient.

IX. Commercial Availability. As implied by the previous discussion, only conventional SIMS is commercially available today. Glow discharge mass spectrometry will soon become available with the introduction of the VG 9000

sold by VG Isotopes of the United Kingdom. Although accelerator-based SIMS is commercially available in concept, the implementation of the instrumentation is a somewhat laborious process and still requires some maturation before it can achieve routine, day-in-day-out utility. Neither time-of-flight SIMS, resonance ionization, multiphoton ionization nor sputtered neutral mass spectrometry are commercially available. The development of a time-of-flight SIMS under this contract could bring forth a commercial instrument, one to three years sooner than would otherwise occur. More importantly, not only would this bring forth a new capability to the materials characterization, materials research community, but the implementation of a time-of-flight SIMS would also hasten the commercial availability of multiphoton ionization and resonance ionization instrumentation.

X. Summary of Strengths and Weaknesses. If we examine each of these evolving techniques, with conventional SIMS as a benchmark, we see that each one has specific capabilities. First, SIMS, as commercially available, is a mature technique which can provide depth profiles and lateral resolutions concomitant with many of the requirements of the semiconductor materials community, has outstanding sensitivity for most elements of interest, and can provide good quantitation, if standards are available. Its most serious limitations are the need for standards in order to provide semiquantitative or quantitative analysis and the prevalence of spectral interferences from molecular ions. Accelerator-based SIMS is a very immature technology for semiconductor analysis although several instruments exist in research laboratories around the world. (None are yet available in the United States.) This technique has the potential for being an extremely valuable technique for the bulk analysis of semiconductor materials. Its quantitative requirements are that of SIMS but that is less of a problem for bulk analysis. Although it has minimal lateral or depth profile capabilities at the present time, its overall potential for a rapid analysis of one or more elements in a material make it a highly viable technique for the bulk characterization of semiconductor material. This potential is borne out by our proposed investigation of this technique.

Looking at the next most mature technique, we find glow discharge mass spectrometry was relatively unheard of a year ago due to of its rather obscure beginning. At the present time, one vendor is offering a glow discharge mass spectrometer, the first instrument to be delivered some time later this year. The technique, although lacking lateral and depth profiling capabilities, will potentially come on line for the bulk analysis of semiconductor material within six to twelve months at a significant level of sophistication. In the short term, it will probably compete with accelerator-based SIMS, since GDMS has the potential for excellent standardless quantitation. Even though GDMS

should meet short term demands for the bulk analysis of semiconductor materials, just as SIMS has for the last five years, we will need some technique three to five years hence, to go below 1ppb or 5×10^{13} at/cm³. Accelerator-based SIMS is presently seen as the technique most probable to meet this need.

The remainder of the techniques of time-of-flight SIMS, resonance ionization mass spectrometry, multiphoton ionization mass spectrometry and sputter neutral mass spectrometry are still immature techniques. We see their potentials for development as the following:

1. Sputter neutral mass spectrometry shows great potential as a microanalytical technique with parts per million detection limits and excellent quantitation. The lateral and depth profiling capabilities should be as good as any of the other techniques, and its only shortcoming will be the potentially reduced sensitivities as compared to the other techniques due to its low overall ionization efficiencies. Thus, SNMS does not vie for the role as the most sensitive for bulk analysis nor does it promise to be the most sensitive in terms of overall efficiency of conversion of atoms into a collectable signal. However, it could become the next versatile technique providing lateral resolutions of the order of one micron, depth resolutions better than presently attainable, sensitivities of a part-per-million and a matrixless, standardless, quantitative capability. Thus, it has the potential for competing with Auger electron spectrometry, scanning Auger microscopy and even perhaps the electron microprobe as a technique of choice in the next five years. To our knowledge there is only one laboratory in the world working on sputtered neutral mass spectrometry, and that is in the laboratory of the developer, Professor Oechsner in West Germany.
2. At the present time, there is only one laboratory actively pursuing multiphoton ionization, Stanford Research Institute. The potential for the technique has yet to be fully achieved, but it does seem that it will provide a moderate quantitative capability, with 0.1 to 1 part per million sensitivities with the ability for lateral and depth profiling analyses dependent upon enhancements to the instrumentation in the ensuing years.
3. Resonance ionization is being pursued in a few laboratories and is nowhere near commercial availability or viability. At the present time its real capabilities lie in its potential for very good detection limits and the absence of spectral interferences. Lateral and depth

profiling resolution capabilities are well into the future, and it will hardly achieve the capabilities of being a rapid survey analytical technique. Its real features lie in the ability to provide exceedingly sensitive, highly selective analyses.

4. Time-of-flight SIMS is presently available in only one laboratory in the world, and it has the potential of being a very viable technique since it combines the ionization and quantitation features of an existing, highly developed technique, conventional SIMS, and the parallel detection capabilities of time-of-flight. Moreover, it should provide very good surface sensitivity and the instrumentation is an ideal foundation for implementing multiphoton ionization or resonance ionization.

Support For Graduate Education at the Oregon Graduate Center
Under a Grant from

CHARLES EVANS & ASSOCIATES

April 1983 - March 1985

Applications of Focused Ion Beams Produced with
Liquid Metal Ion Sources

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Date: 25 April 1985

Introduction

This report, covering the period April, 1983 through March, 1985, describes research work performed by a graduate student supported by this grant at the Oregon Graduate Center. The work related primarily to the application of a liquid metal ion source (LMIS) in a focused beam column to produce a small spot size beam with a high current density.

A high resolution ion beam column had been constructed in the period 1980 - 1981 and which was capable of focusing ≈ 0.3 nA of Ga^+ ion beam current into a spot < 0.5 μmeter in diameter at 15 keV beam energy (current density ≈ 0.2 A cm^{-2}). This focusing column was configured on an ultra-high vacuum system with a precision specimen manipulation stage, a secondary electron collection system and secondary ion optics which included an energy filter and a quadrupole mass spectrometer. In addition, the system contained a low energy electron gun which could be used to discharge insulating specimens. The resulting system provided the means to perform ion microscopy, micromachining and secondary ion mass spectrometry (SIMS) at higher resolution than can usually be obtained. This report describes results achieved with the system over the past two years.

Description of Experimental Apparatus

Most of the apparatus used in this work was of a standard nature which was purchased commercially. This included a Perkin-Elmer/Physical Electronics SIMS II ion collection system, a UTI Quadrupole spectrometer and a model 4700 Galileo Electro-Optics Channeltron^R electron multiplier. The electron flood gun was fabricated from the gun of a CRT. The unique portion of the apparatus, at least in 1983 was the sub-micron capability ion gun. The design of this unit has been described in detail elsewhere¹, as have the liquid metal ion sources used with it². Briefly, it consists of a Ga LMIS which is imaged onto the specimen with a single asymmetric, electrostatic lens through a beam limiting aperture subtending approximately 13 $\mu\text{steradians}$.

The ion beam is deflected and astigmatism corrected with an electrostatic octupole located below the lens. Typical working distances ranged from 25 - 50 mm. The gun could be operated in the energy range 5 - 25 keV. For most applications the ion beam energy was 15 - 20 keV. The focused beam diameter ranged from 0.3 - 0.5 μ meter and the current density on the target from 0.1 to 0.5 A cm⁻².

Applications

A variety of experiments have been conducted using the ion beam system described above. These include micromachining, ion lithography and SIMS. Micromachining experiments and lithography experiments were limited because the ion column did not include blanking plates, however it was possible to test the utility of a relatively low energy beam for exposing resist. In addition, the lithography experiments were useful to study the beam profile.

Work on the possibility of using the LMIS column for SIMS was begun in collaboration with Professor Juergen Schroerer, of Illinois State University, who spent a sabbatical year at OGC in 1983-84. It was necessary to first characterize the energy filter following the secondary ion collection optics in order to determine the collection efficiency and transmission of the system. To this end, an electron impact ionization source was constructed which could be aimed into the collection optics. A gas manifold was built which enabled He, Ne, Ar, Kr or Xe to be admitted into the vacuum system. While it is difficult to determine transmission with great precision, it was found that the band pass of the energy filter was approximately 10 eV and the total transmission from target to detector was 0.2%.

To date, the SIMS instrument has been used to make qualitative and semi-quantitative analyses of conducting and semi-insulating materials. Mass spectra of two NBS Ti alloy samples were obtained which will be compared with those obtained on a CAMECA instrument at the University of Illinois Champagne/Urbana by Professor Schroerer. The utility of e-beam flooding of insulating samples has also been demonstrated, although the effect of e-beam

current density, current and energy have yet to be investigated. It has been shown that the SIMS count rate is drastically affected by charging of insulating samples and that the electron flood gun is essential for investigation of insulators. Most recently, an investigation of contaminants in certain glasses has been undertaken for Tektronix, in which the sub-micron beam spot size has enabled the precise location of the contaminants to be determined, thus demonstrating the usefulness of this approach.

One of the more interesting applications of sub-micron focused ion beams is in lithography. While at first glance it might appear that the utility for lithography of a low energy (< 25 keV) ion beam with a range of only ~ 500 Å would be limited, this turns out not to be the case. Ga of 16 keV energy ions implanted into spin-on-glass (SOG) on photoresist create regions which, to varying degrees, are resistant to reactive ion etching (RIE) with O_2 and plasma etching in CHF_3/O_2 . That is, the Ga implanted regions act as a negative resist. The pattern created by the implanted Ga ions can then be transferred to the underlying photoresist. In this manner it has been possible to fabricate microstructures with high aspect ratios (0.4 μm laterally and 2 μm high) with very smooth walls and excellent linewidth uniformity. This so-called bilevel resist technique is actually an example of maskless ion implantation, not for the doping of semiconductors but rather for the "doping" of resist. By the utilization of the self masking property of implanted Ga, it becomes possible to use the focused ion beam technology to create novel structures. A more complete description of this process will appear shortly¹. Preliminary results have been reported at the Materials Research Society Symposium and will be published in the near future².

A further aspect of ion lithography is its use as a beam diagnostic, principally to determine the current distribution or beam profile. This knowledge turns out to have important ramifications for other uses of focused ion beams such as implantation in semiconductors.

In the area of micromachining, a potentially useful procedure has been demonstrated. The focused ion beam has been used to remove small areas of SiO_2 and Si_3N_4 passivation layers from integrated circuits, in order to render underlying conductors directly visible to an electron beam used for voltage contrast microscopy. Preliminary measurements indicate that unwanted effects of charging of passivation layers can be easily avoided by this technique. In addition, it has been determined under what conditions secondary ion images of passivated (insulating) integrated circuit topology can be obtained without the benefit of charge neutralization. This work has been presented at the SPIE Conference on Submicron Lithography and was published in the Proceedings³. Also, more recent work⁴ indicates that voltage contrast measurements can be made directly with the ion beam, suggesting the exciting possibility of in situ diagnosis and repair (by means of micromachining) of an integrated circuit with the same ion beam.

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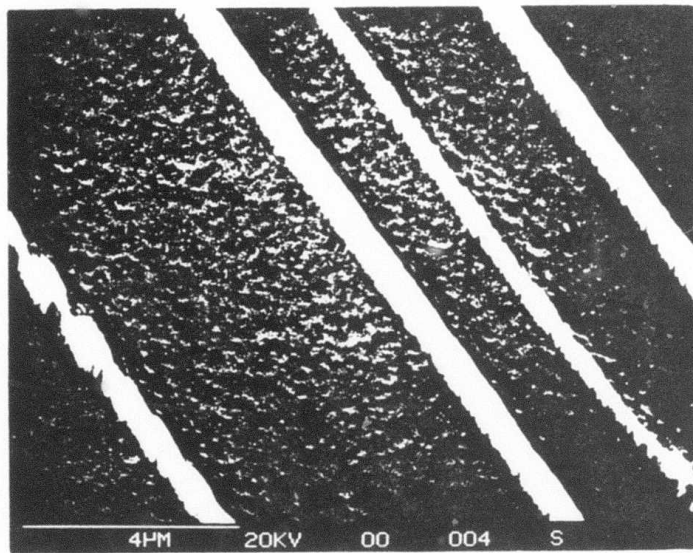


Figure 1. Fine lines ($\sim 0.25 \mu\text{meter}$) patterned in S.O.G. resist to demonstrate that statistical fluctuations in the beam current will appear if the resist is dosed with the minimum charge/cm² necessary for exposure.

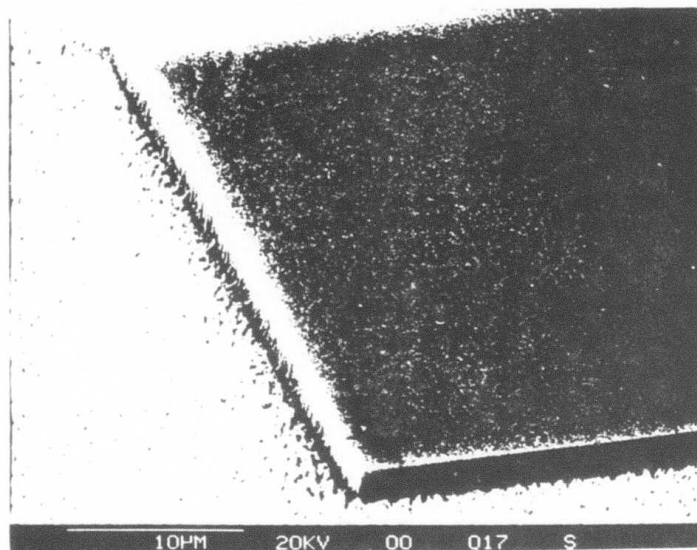


Figure 2. An example of the large, uniform features which can be created by exposing S.O.G. resist with a rastered, sub-micron Ga⁺ ion beam.

An application of focused ion beams to electron beam testing of integrated circuits

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One of the applications of high current density, focused ion beams (FIB) that has been made possible by the advent of the liquid metal ion source (LMIS) is milling of micron sized structures. In this study we examine the prospect of using a FIB system to selectively remove the passivation layer from IC's in order to carry out quantitative voltage contrast measurements on the conductors thus exposed.

Introduction

A focused ion beam can be used to form an image of the surface of a semiconductor device and also to mill through it. If small holes are milled through selected areas of the passivation layer of an integrated circuit (IC), it is possible to make voltage contrast measurements with an electron beam on the conductors beneath the passivation layer.

The primary difficulty in milling small holes through an insulating passivation layer of an IC is encountered at the outset, while attempting to image the features beneath the layer. Since the surface rapidly charges to some positive voltage, the collection of secondary electrons for imaging is often very difficult if not impossible. Contrast mechanisms available in ordinary secondary electron microscopy (SEM) are typically due to the differences in secondary electron yield produced by different materials, topography or potential differences.¹ Under positive ion bombardment of insulators the topographic contrast is often diminished due to the material-dependent surface charging. Since the charging of the insulator is often not uniform due to differences in surface conductivity between inhomogeneous regions, the contrast may be thought of as a type of voltage contrast. For the thin insulating layers on IC's considered here, however, the contrast brought on by surface charging is probably due to the variation in insulator thickness over the underlying circuit, i.e. for a constant surface charge density and dielectric constant, the surface potential is proportional to thickness.

A qualitative picture of transient charging effects of a homogeneous insulator under positive ion bombardment can be formed by considering it as a resistor in parallel with a capacitor. The primary beam current supplies a constant flow of charge to the surface, some of which flows through the resistor. After some time, fixed by the RC time constant, the capacitor will be fully charged and the surface potential will reach an equilibrium value ultimately limited by the beam potential. In practice, the surface potential does not reach beam potential before breakdown on the surface occurs. The time constant will determine the viewing period, unless some method of discharging the surface exists.

Experimental Arrangement

The ion beam column used employs a single, asymmetric electrostatic lens,² with a liquid metal ion source (LMIS) surrounded by a control electrode (suppressor) located 43 millimeters above the lens. An octupole stigmator/deflector element is located below the lens. A diagram of the optical system is shown in Figure 1. V_p is the extraction voltage necessary to operate the LMIS and typically $8 \text{ kV} < V_p < 12 \text{ kV}$, in order to draw the optimum operating current of $\sim 1 \text{ }\mu\text{A}$ from the source. Fine control of the ion current is achieved by means of the voltage V_s on the suppressor electrode. Secondary electrons produced when the ion beam strikes a target are collected and amplified by an electron multiplier, so that the column can be used as a scanning ion microscope. Images are very similar to those produced with a scanning electron microscope.

A LMIS has two important electron optical parameters, the virtual source size δ and the energy distribution, or spread of the beam, ΔE . ΔE has been measured⁴ to be a strong function of the total ion current I_t , whereas δ has been found⁵ to be weakly dependent on current and mass. Because of the rapid increase of ΔE with I_t , it is most advantageous to operate a focused beam system at low values of I_t , $\sim 1 \text{ }\mu\text{A}$, to avoid serious chromatic aberration effects. Even so, the focused spot size is usually chromatic aberration limited.

When material is removed from a surface by sputtering, the rate of removal $dm/dt \sim J$, where J is the focused beam current density and m is the mass removed. The current I_b in the focused spot is the product of the angular intensity of the LMIS, $dI/d\Omega$ ($A\ sr^{-1}$) and the solid angle subtended by the beam limiting aperture $\Delta\Omega = \pi\alpha_0^2$. J is given by $I_b/\frac{\pi d^2}{4}$, where d is the beam diameter, given by

$$d^2 = M^2 \left(\delta^2 + \left(\frac{C_s \alpha_0^3}{2} \right)^2 + \left(C_c \alpha_0 \frac{\Delta E}{E} \right)^2 \right).$$

Here C_s and C_c are the spherical and chromatic aberration coefficients, M the lens magnification, and $E = eV_B$ is the beam energy. Thus,

$$J = \frac{4\ dI/d\Omega}{M^2 \left[\left(\frac{\delta}{\alpha_0} \right)^2 + \left(\frac{C_s \alpha_0^2}{2} \right)^2 + \left(\frac{C_c \Delta E}{E} \right)^2 \right]}.$$

A maximum value for J can be found by differentiating with respect to α , and $J = J_{\max}$ when $\alpha = 1.12 (\delta/C_s)^{1/3}$. Because M , C_s and C_c are all functions of the ratio V_B/V_E , for a given V_B , J increases in value as V_E decreases, even though $dI/d\Omega$ also decreases with V_E at constant I_t .²

Figure 2 is a block diagram of the basic system. The right half shows the scanning and detection scheme. The left half of the figure shows the SIMS system. The extraction optics (EO) transports the secondary ions to the energy analyzer (EA) which presents ions in a 6 eV energy bandwidth to the quadrupole mass analyzer (QUAD) for mass selection. The electron multiplier (EM) amplifies this current which goes either to pulse counting or to analog electronics depending on the output signal strength.

Surface Charging

Surface charge up

In practice the effects of primary beam parameters, e.g. incident particle charge, mass, energy, beam current, current density, and incident angle, target parameters such as mass, surface and bulk conductivities, dielectric constant and degree of homogeneity of the target material will influence the surface charging. In addition, in scanning systems, the scan line time and raster frame rate may be important.⁶ Lastly, a very important factor is the proximity of other electrodes, which not only influences the trajectories of emitted particles but may determine to what extent secondary ions or electrons are able to leave the surface and be collected.

Sputter removal of the target atoms produces both positive and negative secondary ions, secondary electrons, and neutral particles. This results in positive charging since the secondary ion yield δ is usually much less than unity. With electron beam bombardment, there exist two values of the primary beam energy E where $\delta = 1$. The surface potential can be stabilized at the higher value of E since $\partial\delta/\partial E < 0$. Under positive ion bombardment, however, there is no beam energy for which the surface potential is stabilized, since the primary ion current is supplemented by the secondary electron current. Although, in principle, the surface could charge up to the beam potential, in practice the electric fields become large enough to mobilize the surface charge to either move along the surface to seek ground or lower potential depending on the surface conductivity or to flow or discharge to lower potential through the bulk of the material, depending on the bulk conductivity and dielectric constant.

Reduction of surface charging

One method of reducing the positive charging due to the ion beam is to bombard the surface with negatively charged particles, either electrons or negative ions. From the standpoint of charge neutralization, whether the neutralizing current or current density is important will depend on the surface conductivity. Another method utilizes the fact that the impinging metallic ions could reduce the charging by some form of induced conductivity. This method has been used successfully with Cs^+ ions in the SIMS analysis of insulating crystals.⁷ In one sense, the requirements for imaging an insulating surface are less critical than those for producing an accurate SIMS spectrum, since trajectories altered by surface charging are tolerable as long as the secondary currents can be collected.

Experimental findings

Imaging the insulating layer

Since ion bombardment of surfaces produces both secondary electrons and secondary ions, either can be used for imaging. However, surface charging may make it impossible to image with electrons.

Figures 3a and 3b show secondary electron images obtained with a Ga^+ focused ion beam. The target is an unpackaged Large Scale Integration (LSI) multiplier chip for which the input, output, and power supply pins were electrically floating. Since positive ion bombardment of the insulating passivation layer results in a positive surface potential, the image is detectable only during the transient charge-up time. For a primary Ga^+ ion beam current of 3×10^{-10} A at $E = 4$ keV and +250 volts bias on the CEM, the time constant for charging is of the order of seconds. The Figure 3a image lost sufficient contrast after 5 seconds to preclude seeing the circuit detail. After 13 to 15 seconds out of the field of view of the scanning ion beam, the passivation layer had discharged sufficiently so the process could be repeated. This reversible phenomenon could be repeated indefinitely. Figure 3b depicts a similar effect. In this case, the average current density was increased by a factor of 25 by decreasing the area by a factor of 25 and the time required to achieve the same loss of image contrast was estimated to be less than one second. (This is indicated by the small dark area at the right of center of the micrograph.) The final image was then obtained at the same magnification used to obtain Figure 3a.

The difficulty of imaging details with secondary electrons under ion bombardment through a passivation layer increases as the thickness of the layer increases, and becomes acute when the thickness exceeds $1 \mu\text{m}$. Figure 4a shows a secondary electron image of a portion of a dual quad NOR gate. The insulating layer thickness is estimated to be $1 \mu\text{m}$ or less. Figure 5, on the other hand, is a low voltage SEM image of a 64 K dynamic RAM which proved impossible to image by secondary electrons produced under ion bombardment. The passivation layer for this device consists of a nitride layer over an oxide layer with a total thickness of $1.5 \mu\text{m}$ to $2 \mu\text{m}$. For the case of imaging by secondary ions, however, it becomes possible to see image contrast after several minutes of bombardment with the Ga^+ ion beam even for relatively thick layers.

Milling of insulating layers

When the surface topography of the passivation layer can be imaged it becomes possible to remove selected areas of it. Figures 6-8 show square holes produced by raster scanning the Ga^+ ion beam over the runs of a dual input, quad NOR gate. The holes shown in Figure 7 took 15 seconds to produce, are $0.8 \mu\text{m}$ square, and were milled using an average current density (beam current/raster area) of $\sim 50 \text{ mA/cm}^2$. This corresponds to a sputtering rate of 700 \AA/sec with a passivation layer thickness of $\sim 1 \mu\text{m}$. The holes shown in Figures 7 and 8, though somewhat larger were made under similar conditions. For these cases there appears to be no adverse effect of charging on the milled shape. However Figure 9, which is a low voltage SEM image of a resistor covered by an oxide passivation layer, indicates some shape distortion for the large $10 \mu\text{m}$ hole. Since the charging effects are material dependent, it is difficult to say exactly why the shape is not precisely square. Generally, one can say that the interplay of sputtering and charging will determine to what extent the primary beam deflection may be altered. This problem has not been explicitly examined.

It is important to note that a simple method exists for determining when a hole has been milled completely through the passivation layer, if the underlying conductor is grounded. There is a large change in image contrast present at the moment of breakthrough due to the large yield of secondary electrons from the conducting layer, as shown in Figures 10a and 10b. Since the penetration depth for these heavy ions is $\sim 150 \text{ \AA}$ at 20 keV, the effect of ion bombardment will be negligible until the $1 \mu\text{m}$ thick insulation is virtually entirely sputtered through. This suggests the use of SIMS as an additional technique to monitor the milling of the passivation layer.

Voltage contrast of ion milled passivated IC's

Figures 11a and 11b are SEM images of the milled region of a $3.9 \mu\text{m} \times 3.9 \mu\text{m}$ square hole in two voltage states. With positive voltage applied to the metal run, the image is dark (Figure 11a) while the bright image (Figure 11b) is obtained with the run grounded. These images clearly show the voltage contrast effect.

Figure 12 shows the result of a simple measurement of a resistor covered with $\sim 1 \mu\text{m}$ of SiO_2 (seen in Figure 9). In this case, a 1 Hz, 1 volt square wave was applied to one pad of the resistor with the other pad kept at ground. The figure shows a comparison of the voltage measured with the VCSEM through the passivation layer (curve 1) with the same measurement made through the ion milled hole shown in Figure 9 (curve 2). It clearly

indicates the effect of surface charging under the electron beam as the measurement is made.

Figure 13 shows the secondary electron energy distribution which is obtained by differentiating the output of the secondary electron energy analyzer. The measurement over the passivation layer (curve 1) is shifted ~ 1.3 V negative with respect to the measurement through the hole (curve 2). However the structure on the right half of each curve is probably an artifact.

Conclusions

We have demonstrated the potential utility for voltage contrast microscopy of milling small ($0.8 \mu\text{m} - 10 \mu\text{m}$) holes through the passivation layers of integrated circuits, using a focused ion beam. We have also observed the effect of surface charging on the ability to image the topography of the passivation layer of IC's. For thin layers, both secondary electron and secondary ion images can be obtained. For thicker layers however, only ion images are obtainable after several minutes of ion beam bombardment.

Voltage contrast measurements were made on circuits with milled areas in the passivation layer. Preliminary results indicate the charging problem is reduced for measurements made through the milled holes.

The problem of surface charging is significant for a passivation layer thickness $> 1 \mu\text{m}$ and will require a charge neutralization technique to be developed, in order that focused ion beams can be used for high resolution imaging or milling of insulating surfaces.

Lastly, we note that the most important consideration for the successful application of the technique to IC device testing is the effect of ion milling on device performance. Although this has not been systematically examined, our experience indicates that some devices survive long periods of ion bombardment while others do not. This problem should be studied to determine precisely under what bombardment conditions and for which types of IC's this ion beam milling can be applied.

Acknowledgment

The authors wish to acknowledge the Murdock Charitable Trust Foundation for support of this work.

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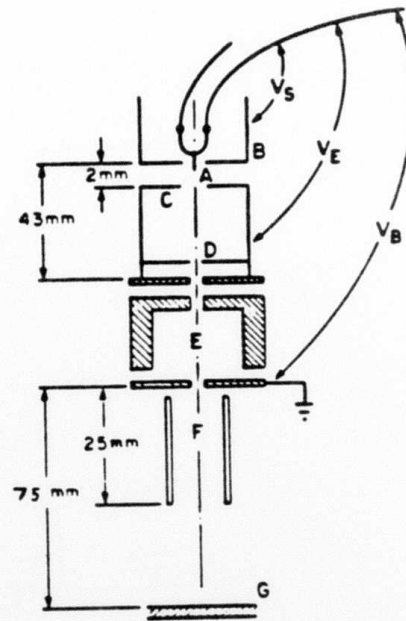


Figure 1. Schematic diagram of the optical column for the focused ion beam column. A = LMIS, B = suppressor, C = extraction electrode, D = beam limiting aperture, E = electrostatic lens, F = octupole, G = target. Voltages V_S , V_E and V_B are measured between points shown.

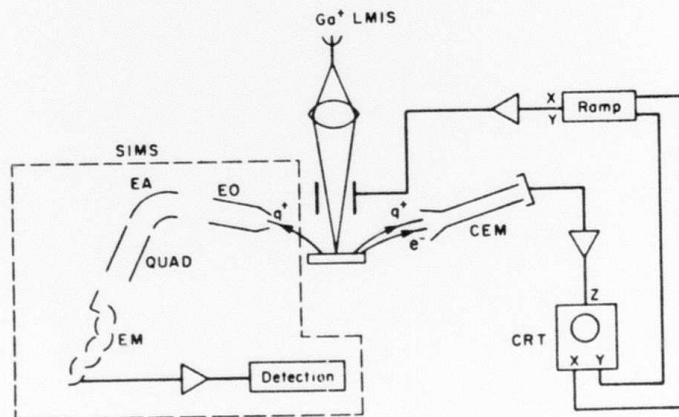
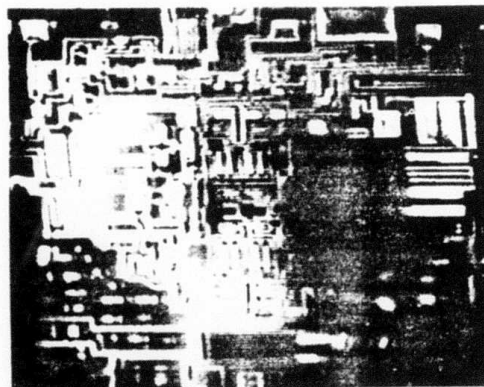
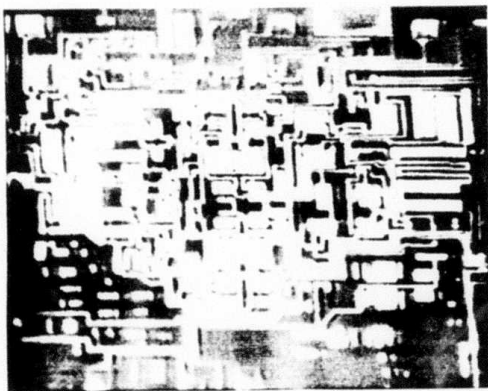


Figure 2. Block diagram of the complete system including SIMS. The ramp generator simultaneously drives the CRT and octupole stigmator/deflector. The secondary charged particles are collected and multiplied in the electron multiplier (SEM). The CEM output modulates the intensity axis of the oscilloscope. EO = SIMS extraction optics, EA = energy analyzer, QUAD = quadrupole mass analyzer, EM = 16 dynode Cu/Be electron multiplier.



Figures 3a and 3b. Transient secondary electron images under Ga^+ ion bombardment.



Figure 4. Scanning ion microscope (SIM) photos of IC with passivation layer; (a) image from secondary electrons; (b) image from secondary ions.

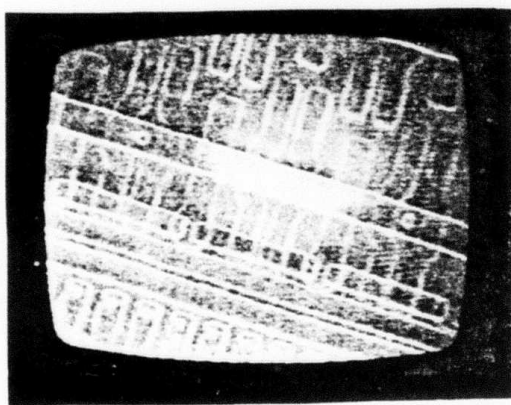


Figure 5. SEM image of 64 K DRAM at ~ 3 keV beam energy.

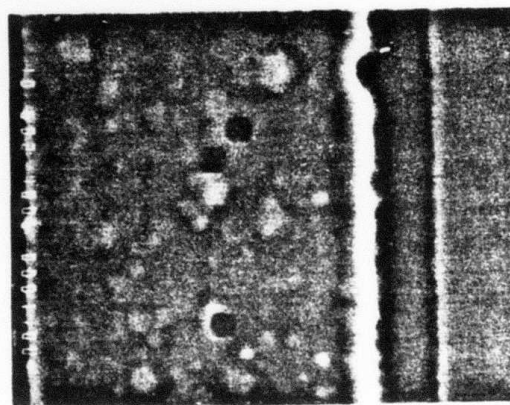


Figure 6. SEM photo of $0.8 \mu\text{m}$ holes milled with Ga^+ ion beam.

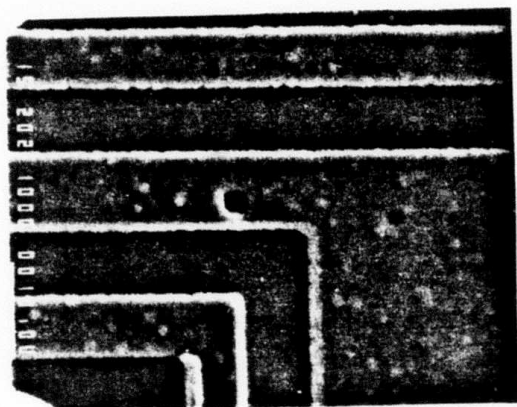


Figure 7. SEM photo of milled areas. Large square $\sim 2 \mu\text{m}$. Small square $\leq 1 \mu\text{m}$.

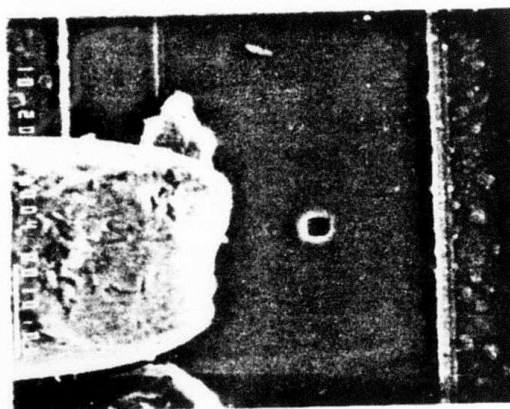


Figure 8. SEM photo of $2 \mu\text{m}$ hole.

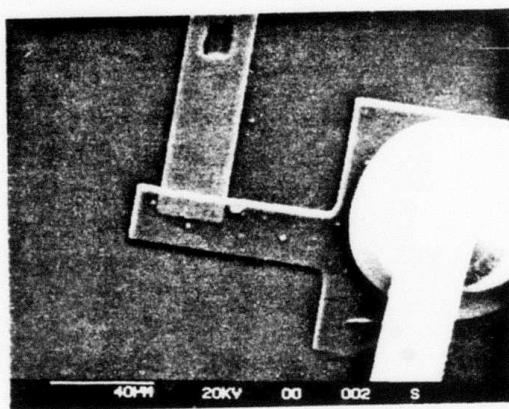
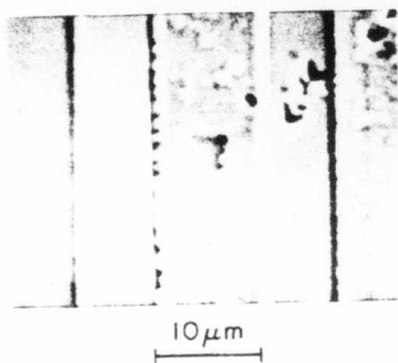
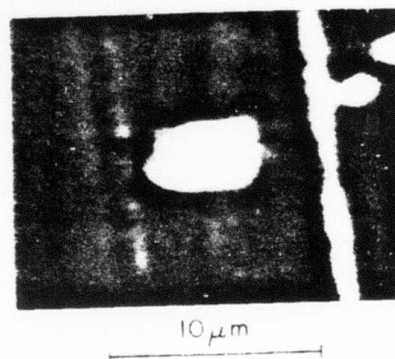


Figure 9. SEM photo of large ($10 \mu\text{m}$) milled area.

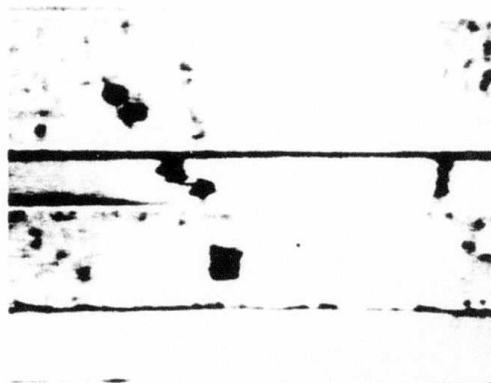


(a)



(b)

Figure 10. Photos of IC with $3.9 \text{ by } 3.9 \mu\text{m}$ hole milled through passivation layer (a) SEM photo; (b) SIM photo.



(a)



(b)

Figures 11a and 11b. SEM photo of IC run with $3.9 \mu\text{m} \times 3.9 \mu\text{m}$ hole milled through the passivation layer; (a) positive voltage on run; (b) run grounded.

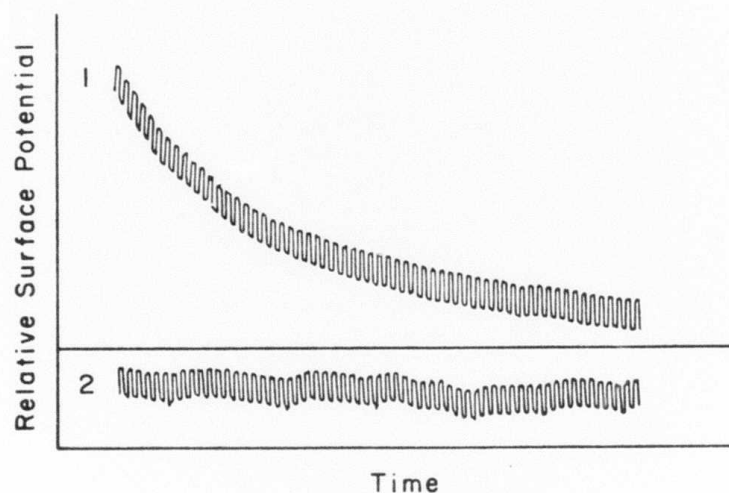


Figure 12. Curve (1) shows the effect of charging on voltage measurement taken through the passivation layer of the Figure 9 resistor. Curve (2) was obtained through the milled area.

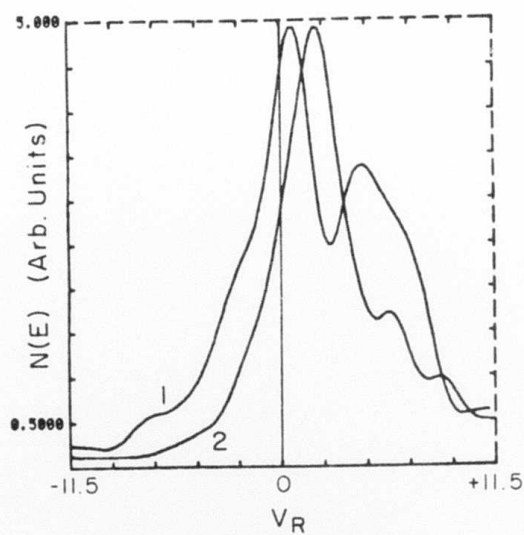
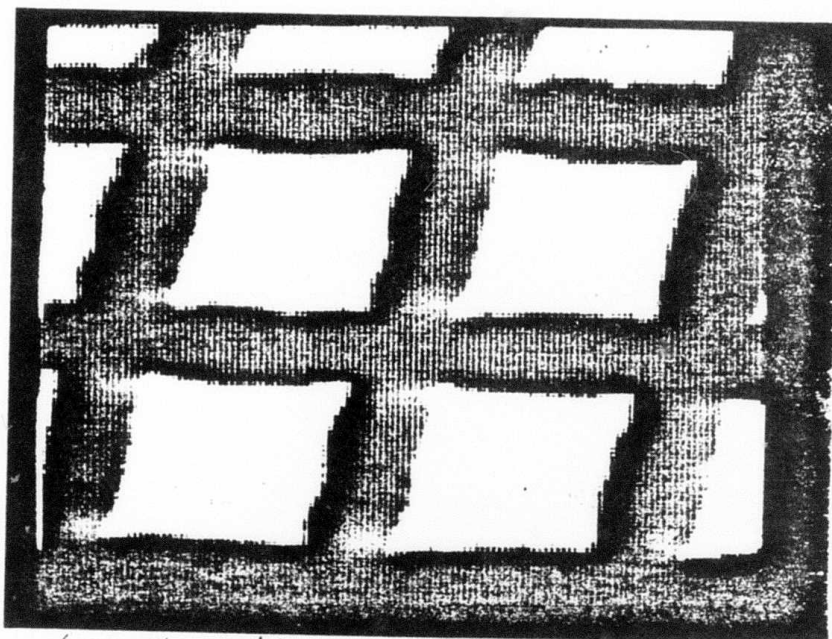
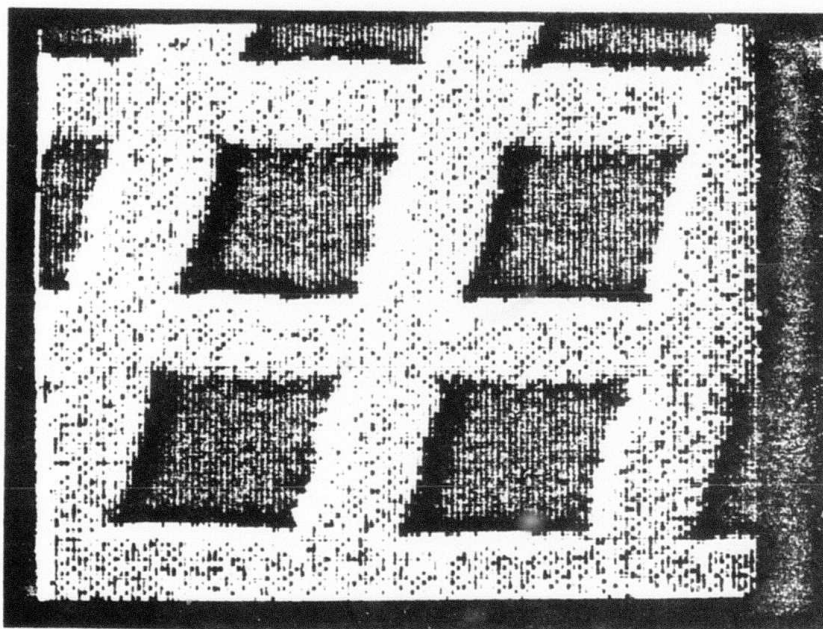


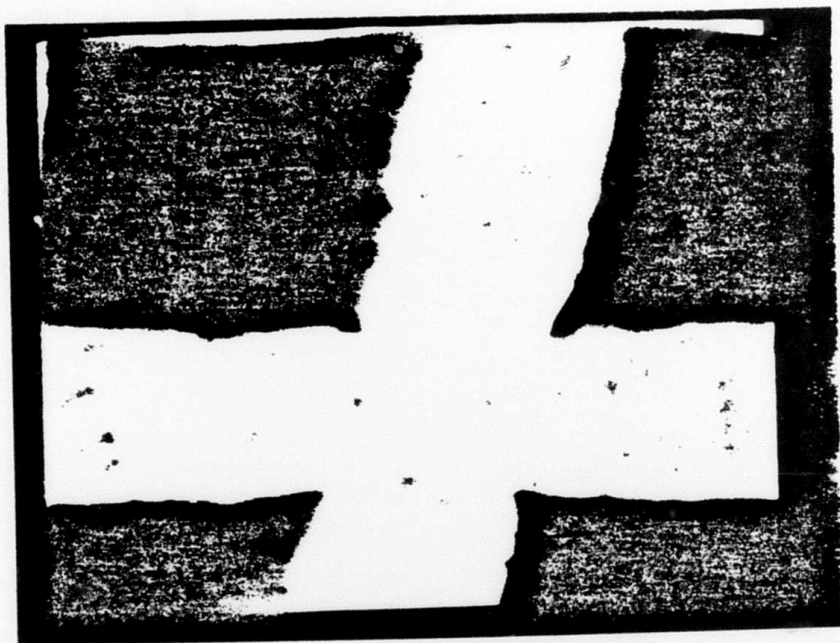
Figure 13. Secondary electron energy distribution taken through the passivation layer (1) and milled area (2) of the Figure 9 resistor.



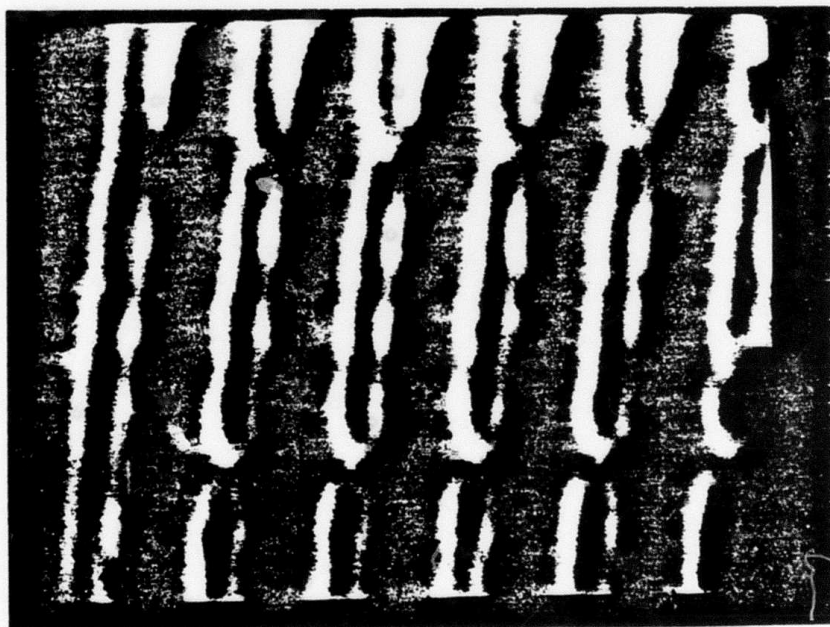
6 μ m Ni on Al Al⁺ SIMS image



6 μ m Ni on Al SIMS IMAGE OF N⁺



60m Ni sec. elec. image



1 Ni 21 Lines

